

# Dopant effect on point defect incorporation into growing silicon crystal

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Acceptor and donor dopants affect the critical ratio  $v/G$  for the change-over from interstitial to vacancy incorporation ( $v$  is the growth rate and  $G$  is the near-interface temperature gradient) in growing silicon crystals. The boron effect (an increase in the critical  $v/G$ ) is nicely accounted for by a simple mechanism of electronic shift in the equilibrium concentrations of the charged point defects at the melting point ( $T_m$ ). By fitting the theoretical curve to the experimental data, the ratio of the equilibrium concentrations of vacancy and self-interstitial is defined to be 1.3 at  $T_m$ . Given this the interstitial diffusivity and the two equilibrium concentrations at  $T_m$  can then be specified. Beside the electronic shift, alternative mechanisms (interstitial impurity component, impurity pairing to vacancy) are discussed to provide a general formula for the impurity-induced shift in the critical  $v/G$ . © 2000 American Institute of Physics. [S0021-8979(00)02108-3]

## I. INTRODUCTION

Incorporation of intrinsic point defects, vacancy, and self-interstitial, into growing silicon crystals is controlled by the growth rate ( $v$ ) and the axial temperature gradient ( $G$ ) in the vicinity of the crystal/melt interface.<sup>1,2</sup> The defect transport equations generally include both parameters,  $v$  and  $G$ , but for particular assumptions (fast recombination, equilibrium boundary conditions at the interface), the problem includes only one parameter combination,  $v/G$ . If this ratio exceeds some critical value,  $\xi_t$ , the incorporated defects are vacancies while the interstitial concentration vanishes fast upon lowering the temperature. At  $v/G < \xi_t$ , the incorporated defects are self-interstitials while the vacancy concentration vanishes fast with decreasing temperature. The critical ratio  $\xi_t$  is expressed<sup>1,2</sup> through the point defect parameters at the melting point,  $T_m$ .

At some lower  $T$ , the incorporated defects agglomerate into detectable structural microdefects: vacancies normally give rise to octahedral voids,<sup>3-5</sup> while interstitials produce dislocation loops.<sup>6,7</sup> The microdefect type follows the “ $v/G$  rule:” voids are formed at higher  $v/G$  while the loops are formed at lower  $v/G$ .

When  $v/G$  is close to the critical ratio, the incorporated defect concentration is relatively low which results in a drastic change in the microdefect type. Particularly at  $v/G$  slightly larger than  $\xi_t$  (thus low vacancy concentration) oxide particles are produced instead of voids in the course of vacancy agglomeration.<sup>8</sup> For this reason, the main vacancy-containing region of a crystal (where voids are formed) is surrounded with a narrow marginal band containing oxide particles. This “ $P$  band” gives rise to a so-called oxidation-induced-stacking-fault ring<sup>9,10</sup> (an OSF ring) found after wafer oxidation. There is normally a pronounced radial variation in  $G$ , and a corresponding variation in  $v/G$  along the interface. This can produce crystals of a “mixed type” containing a vacancy core surrounded with a peripheral intersti-

tial region. The OSF ring is a useful marker of the vacancy/interstitial boundary. Although it is located within the vacancy core, it is close to the boundary. Tracing the position of the OSF ring<sup>11</sup> under various growth conditions has shown that it obeys the  $v/G$  rule: the ring corresponds to a particular local value  $\xi_r$  of this ratio, about 0.13 mm<sup>2</sup>/min K. This number is expected to be only slightly larger than the critical ratio,  $\xi_t$ .

## II. DOPANT EFFECT ON GROWN-IN MICRODEFECTS

It has long been known that microdefect formation in both Czochralski (CZ) and float-zoned (FZ) silicon crystals is affected by doping with conventional donors or acceptors.<sup>12,13</sup> The CZ crystals studied in Ref. 12 were of small diameter (40 mm) and were grown accordingly under conditions of high axial temperature gradient (about  $G=14$  K/mm at the interface). The critical rate,  $v_t=G\xi_t$ , for the change over from interstitial to vacancy incorporation is between 1 and 2 mm/min for this case. In crystals grown at  $v=2$  mm/min, the microdefects (which are voids according to the modern view) were suppressed by acceptor (boron, gallium) doping. In crystals grown at  $v=1$  mm/min, the microdefects (loops) were suppressed by donor (antimony, phosphorus, and arsenic) doping. The tin impurity (of the largest atomic size) had no effect showing that the impurity-induced strain is irrelevant. Similar results were obtained<sup>13</sup> for acceptor, donor, and tin-doped FZ crystals.

These data indicate to a dopant-induced shift in the critical  $v/G$  ratio—an upward shift due to acceptor dopants, a downward shift due to donor dopants; however, little quantitative information can be derived. Recently, the effect of boron on the position of the OSF ring was studied in detail,<sup>14</sup> and it was found that  $v/G$  ratio corresponding to the ring position ( $\xi_r$ ) is indeed shifted upward, roughly in proportion to the dopant concentration  $N$ :

$$\xi_r/\xi_{r0} = 1 + N/N_c, \quad (1)$$

where  $\xi_{r0}$  corresponds to undoped material; the characteristic concentration  $N_c$  causing a strong shift is  $1.12 \times 10^{19} \text{ cm}^{-3}$ . The relative shift in the critical ratio,  $\xi_t/\xi_{t0}$ , is described by the same relation since  $\xi_t$  is close to  $\xi_r$ .

### III. ELECTRONIC SHIFT IN THE EQUILIBRIUM POINT DEFECT CONCENTRATIONS AS THE CAUSE FOR THE DOPANT EFFECT

Both the vacancy and self-interstitial are charged defects; the charge state is dependent on the Fermi level position.<sup>15</sup> Particularly, in material of intrinsic conductivity (at the Fermi level close to the midgap), the prevailing charge state of a vacancy is expected to be single negative. The prevailing charge state of a self-interstitial is neutral, with a small contribution of double-positive charge (the single-charge state is practically absent due to a so-called “negative- $U$ ” sequence of energy levels<sup>15</sup>).

A dopant (acceptor or donor) introduced up to the concentration  $N$ , induces some shift in the electron concentration  $n$  (and in the hole concentration  $p$ ) with respect to the initial intrinsic value,  $n_0$ . The electron/hole equilibrium relation,  $pn = n_0^2$ , together with the neutrality condition  $p - n = N$  (for acceptor dopant) provides an explicit expression for a shifted electron concentration:

$$n = -N/2 + (N^2/4 + n_0^2)^{1/2}. \quad (2)$$

For donor doping ( $n - p = N$ ), one should replace  $N$  with  $-N$  in this expression.

The intrinsic electron concentration,<sup>16</sup> when extrapolated to the melting point, amounts to  $4.2 \times 10^{19} \text{ cm}^{-3}$ . This number is considerably larger than a typical doping level  $N$  (normally well below  $10^{19} \text{ cm}^{-3}$ ). Therefore, the shift in  $n$  is relatively small, and the expression (2) is reduced to

$$n = n_0 \pm N/2, \quad (3)$$

where the plus or minus sign stands for donor or acceptor doping, respectively.

The defect equilibrium concentration  $C_z$  of a particular charge state  $z$  (of  $z$  elementary positive charges) is shifted in proportion to  $n^{-z}$ . This follows simply from the mass action law for the defect introduction into lattice: one defect is accompanied by  $z$  electrons, and the product  $C_z n^z$  is a constant. The total equilibrium defect concentration  $C_e$  is then

$$C_e = \sum C_{z0} (n/n_0)^{-z}, \quad (4)$$

where the sum is over all the possible charge states  $z$  (generally both positive and negative) and  $C_{z0}$  refers to the intrinsic (undoped) material. Since the  $n/n_0$  ratio, as defined by Eq. (3), is close to 1, the factor  $(n/n_0)^{-z}$  can be expanded to be  $1 + zN/2$  for acceptor doping. The final expression for a shift in the total equilibrium defect concentration caused by acceptor doping is

$$C_e = C_{e0} (1 + ZN/2n_0), \quad (5)$$

where  $Z$  is the average defect charge (in elementary charge units) for the intrinsic material,  $Z = \sum z C_{z0} / \sum C_{z0}$ . The expression (5) is valid both for vacancy (the average vacancy

charge  $Z_v$  is close to  $-1$ ) and for self-interstitial (the average interstitial charge  $Z_i$  is positive but small, and so can be put zero).

A relative shift in the equilibrium concentration of point defects, as defined by expression (5), is small at  $T_m$  since  $N \ll n_0$ . It is, however, enough to cause an appreciable shift in the critical  $v/G$  ratio. This conclusion follows from the explicit expression<sup>1,2</sup> for the critical ratio:

$$\xi_t = (E/kT_m^2)(D_i C_{ie} - D_v C_{ve}) / (C_{ve} - C_{ie}), \quad (6)$$

where the equilibrium concentrations of vacancy and interstitial ( $C_{ve}$  and  $C_{ie}$ ) and their diffusivities ( $D_v$  and  $D_i$ ) refer all to the melting point  $T_m$ , and  $E$  is the defect formation energy averaged over the two species. The expression (6) is somewhat simplified to neglect a possible contribution of defect drift induced by the temperature gradient. The essential point is that both the expression (6) and the more general expression (taking the drift into account<sup>2</sup>) include the concentration difference  $C_{ve} - C_{ie}$  in the denominator. This difference is relatively small (the two concentrations  $C_{ve}$  and  $C_{ie}$  are very close one to the other<sup>2</sup>). Even a small shift in either of the two concentrations may therefore cause an appreciable shift in  $C_{ve} - C_{ie}$ , and accordingly a strong shift in the critical  $v/G$  ratio.

The shift in the denominator of Eq. (6) provides the major contribution to the dopant effect. In the numerator the interstitial term  $D_i C_{ie}$  strongly dominates<sup>2</sup> over the vacancy term  $D_v C_{ve}$ . A small electronic shift in  $D_i C_{ie}$  (generally caused by a shift in both  $C_{ie}$  and  $D_i$ ) is therefore of minor importance. We will thus take into account only the major effect that caused by shifting the equilibrium difference  $C_{ve} - C_{ie}$ . On substituting the shifted equilibrium concentrations from Eq. (5) into the denominator of Eq. (6), one gets the final expression for the relative “electronic” shift in  $\xi_t$  induced by acceptor doping:

$$\xi_t/\xi_{t0} = 1/(1 - KN), \quad (7)$$

with the coefficient  $K$  expressed through the melting point concentration ratio  $c = C_{ve}/C_{ie}$  (for undoped material):

$$K = (1/2n_0)(Z_i - cZ_v)/(c - 1). \quad (8)$$

The expression (7) applies also to donor doping if  $N$  is replaced with  $-N$ .

Even if the acceptor dopant concentration is as small as 10% of  $n_0$  ( $\sim 4 \times 10^{18} \text{ cm}^{-3}$ , a typical doping level), the relative electronic shift in  $\xi_t$  is on the order of 20%–50%, for a reasonable range<sup>2</sup> of  $c$  between 1.1 and 1.4. The experimental shift Eq. (1) induced by boron is of the same order. The electronic effect on the equilibrium concentrations of point defects (actually on the vacancy concentration) is then a reasonable explanation of the boron-induced shift in  $\xi_t$ . Theoretical curves for the relative shift are plotted in Fig. 1, according to the expressions (7) and (8) where three values for the concentration ratio  $c$  were tried ( $c = 1.2, 1.3$ , and  $1.4$ ). The circles in this figure represent the experimental data for boron.<sup>14</sup> Since the theoretical curve is so sensitive to the assumed  $c$ , the experimental data allow a good fitting of the concentration ratio  $c$ . It is close to 1.3, with an uncertainty of  $\pm 0.05$ . Strictly speaking, it is the coefficient  $K$  in Eq. (7) that

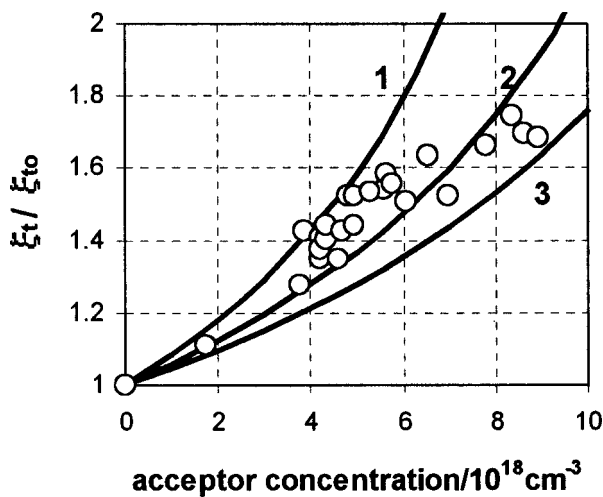


FIG. 1. Relative shift in the critical  $v/G$  ratio caused by an acceptor dopant through the electronic shift in the point defect equilibrium concentrations at the melting point. The curves 1, 2, and 3 are computed for the three representative values of the vacancy-to-interstitial concentration ratio ( $c=1.2$ , 1.3, and 1.4, respectively). The circles represent the experimental data for boron (see Ref. 14).

was fit to be  $5.2 \times 10^{-20} \text{ cm}^{-3}$ . The concentration ratio  $c = 1.3$  was then deduced from the expression (8). This number relies on the assumed numbers for  $n_0$  and for the average charges  $Z_v$  and  $Z_i$ . The theoretical downward shift is predicted for donor doping by expressions (7) and (8) with  $N$  now replaced by  $-N$ . This shift is shown in Fig. 2 for the best fit value of the coefficient  $K$ .

#### IV. POINT DEFECT PARAMETERS

The deduced concentration ratio ( $c = C_{ve}/C_{ie} = 1.3$ ) can be now used to specify the other point defect parameters at  $T_m$ . The interstitial diffusivity  $D_i$  can be expressed through the critical  $v/G$  ratio (which is close to  $0.12 \text{ mm}^2/\text{min K} = 2 \times 10^{-5} \text{ cm}^2/\text{s K}$ ) from the basic expression (6):

$$D_i = D_v c + \xi_{i0} (kT_m^2/E)(c-1). \quad (9)$$

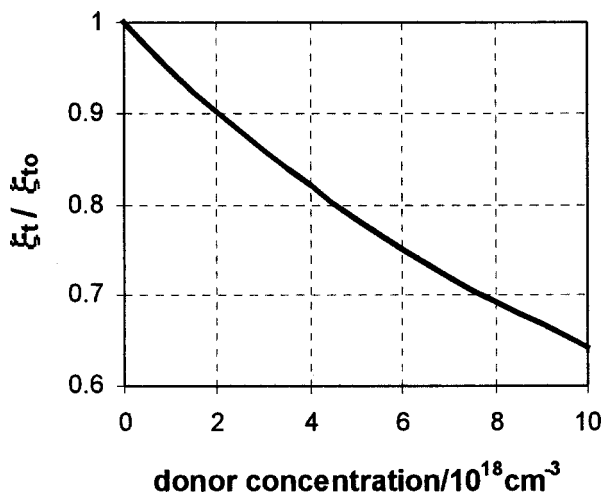


FIG. 2. Relative "electronic" shift in the critical  $v/G$  ratio predicted for donor doping.

The vacancy diffusivity provides only a minor contribution to the right-hand part, and an approximate estimate<sup>2,8</sup> ( $D_v = 5 \times 10^{-5} \text{ cm}^2/\text{s}$ ) is sufficient for a good evaluation of  $D_i$ . Assuming the most reasonable number<sup>2</sup> for the average formation energy ( $E=4.5 \text{ eV}$ ), one gets  $D_i = 3.9 \times 10^{-4} \text{ cm}^2/\text{s}$ . The self-diffusion product  $D_i C_{ie}$  was found<sup>2</sup> to be around  $3 \times 10^{11} \text{ cm}^2/\text{s}$  at  $T_m$ . Accordingly, the interstitial equilibrium concentration  $C_{ie}$  is thus found to be about  $7.7 \times 10^{14} \text{ cm}^{-3}$ . The vacancy equilibrium concentration  $C_{ve}$  is larger by a factor of  $c$  (1.3) and thus equals  $10^{15} \text{ cm}^{-3}$ . The concentration difference,  $C_{ve} - C_{ie} = 2.3 \times 10^{14} \text{ cm}^{-3}$ , is a measure for the incorporated vacancy concentration, and thus for the amount of vacancies stored in voids. This number is in accord<sup>2,17</sup> with the data on the void density and volume.

#### V. DISCUSSION

It is now clear that the boron effect on the critical  $v/G$  ratio can be well explained by a slight electronic shift in the point defect equilibrium concentrations at the melting point. Therefore, there is no need to invoke other possible mechanisms for the boron effect (and, probably, for all the other acceptor and donor dopants). We will, however, briefly discuss alternative explanations for the dopant-induced shift in  $\xi_t$ .

An alternative mechanism for the boron-induced shift is the presence of a small fraction of interstitial boron, along with the prevailing substitutional state.<sup>18</sup> The total number of excess atoms (with respect to the lattice with all sites filled) is now equal to  $C_i - C_v + N_i$ , where  $C_v$  is the vacancy concentration,  $C_i$  is the self-interstitial concentration, and  $N_i$  is the interstitial boron concentration. This combination of three concentrations is a reaction invariant. It is not changed by the recombination of any interstitial with a vacancy or by the kick-out reaction (replacing one type of an interstitial with another). The critical  $v/G$  ratio corresponds to the condition of zero total flux of excess atoms into the crystal bulk. The main difference from the undoped crystal is that the convection flux  $v(C_i - C_v)$  is replaced with  $v(C_i - C_v + N_i)$ . Accordingly, the interstitial boron concentration  $N_i$  must be added to  $C_{ie}$  in the denominator of Eq. (6). Since  $N_i$  (at  $T_m$ ) is proportional to the total boron concentration ( $N_i = R_i N$ , where  $R_i$  is the equilibrium interstitial boron fraction), the two effects, that by interstitial boron and that by electronic shift in  $C_{ve}$  and  $C_{ie}$ , are simply summed. The overall shift is then defined by the previous expression (7), with the coefficient  $K$  replaced by  $K + R_i/(C_{ve} - C_{ie})$ . The interstitial boron contribution is insignificant if  $R_i \ll 10^{-5}$ .

Another possible mechanism of the shift in  $\xi_t$  is pairing of vacancies with substitutional impurity atoms. Here, the invariant combination of the concentrations is  $C_i - C_v - N_v$ , where  $N_v$  is the concentration of vacancy-impurity pairs. Accordingly, the expression (6) is modified by adding  $R_v N$  (where  $R_v$  is the equilibrium fraction of impurity atoms paired with vacancies at  $T_m$ ) to the vacancy concentration

$C_{ve}$ . The critical  $v/G$  ratio is shifted downward by this effect. The overall downward shift caused by donor doping is a combined effect of the electronic shift and vacancy/impurity pairing. It is again described by the expression (7), where  $K$  is replaced with  $-K - R_v / (C_{ve} - C_{ie})$ .

Generally, if both interstitial impurity atoms and impurity-vacancy pairs are important, the explicit impurity correction in the denominator of Eq. (6) is  $R_v N - R_i N$ , and must be added to the implicit electronic correction. The overall shift in the critical  $v/G$  can be then written in a general form applicable for acceptor, donor, and neutral dopant:

$$\xi_t / \xi_{t0} = 1 / \{1 + [Z_d K + (R_v - R_i) / (C_{ve} - C_{ie})] N\}, \quad (10)$$

where  $Z_d$  is the dopant charge ( $-1$  for acceptor,  $1$  for donor,  $0$  for neutral dopant). An example of a neutral dopant causing an appreciable shift in  $\xi_t$  is carbon. It was found<sup>13</sup> that carbon doping up to  $1.7 \times 10^{17} \text{ cm}^{-3}$  can change the material type from vacancy to interstitial. This means an appreciable upward shift in  $\xi_t$ . The coefficient  $R_i - R_v$  for carbon can be estimated to be on the order of  $3 \times 10^{-4}$ .

For acceptor dopants, the electronic contribution to  $\xi_t$  is universal, while the “chemical” contribution,  $(R_i - R_v) / (C_{ve} - C_{ie})$ , is specific for a particular impurity. Thus, if the acceptor-induced shift is found to be independent of the impurity kind, then the dominance of the electronic effect is

proven. The same assumption for the donor dopants may be tested in a similar fashion.

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