

# Gigantic uphill drift of vacancies and self-interstitials in silicon

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## ABSTRACT

Point defect transport in a growing crystal includes a drift along the temperature gradient,  $G$ , at a velocity  $\alpha G$ . It was not clear if the drift is negligible or strong in silicon crystal growth. It is now found that reported microdefect patterns in crystals grown with a temporarily halt provide a clear evidence in favour of a strong (even gigantic) drift of both kinds of intrinsic point defects. The drift coefficients  $\alpha_V$  (for vacancies) and  $\alpha_I$  (for self-interstitials) are deduced by fitting the simulating defect profiles to the observed location of halt-induced interstitial region immersed into a vacancy-type crystal.

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## 1. Introduction

The incorporated concentration of the intrinsic point defects, either vacancies (V) or self-interstitials (I), is controlled by the defect transport and by the recombination of V and I. The transportation is by diffusion, by crystal movement at a velocity  $V$ , and also by a drift along the temperature gradient  $G$ . In a steady-state growth mode and in a 1D approximation, the type of incorporated defect is V if the ratio  $V/G$  is above some critical value  $(V/G)_{cr}$ . Otherwise – at lower  $V/G$  – the type of incorporated defects is I. The critical ratio  $(V/G)_{cr}$  that separates the V-mode of crystal growth from the I-mode is expressed [1] through the defect parameters (including those for the drift) taken at the melting point ( $T_m$ ).

The drift velocity, proportional to the gradient of the inverse temperature and scaled to the defect diffusivity  $D$  can be written [1] as

$$V_{drift} = -D \text{grad} \left( \frac{\varepsilon}{kT} \right) \quad (1)$$

the “drift energy”  $\varepsilon$  is a kinetic parameter that can be of any value and sign; positive sign means an uphill drift—from a colder to a hotter crystal part. For particular temperature profile, when  $1/T$  is a linear function of the axial distance  $z$  (which means that  $1/T = 1/T_m + Gz/T_m^2$ ) the drift velocity is reduced to  $-\alpha G$  where the drift

coefficient  $\alpha$  is expressed through  $D$  and  $\varepsilon$ :

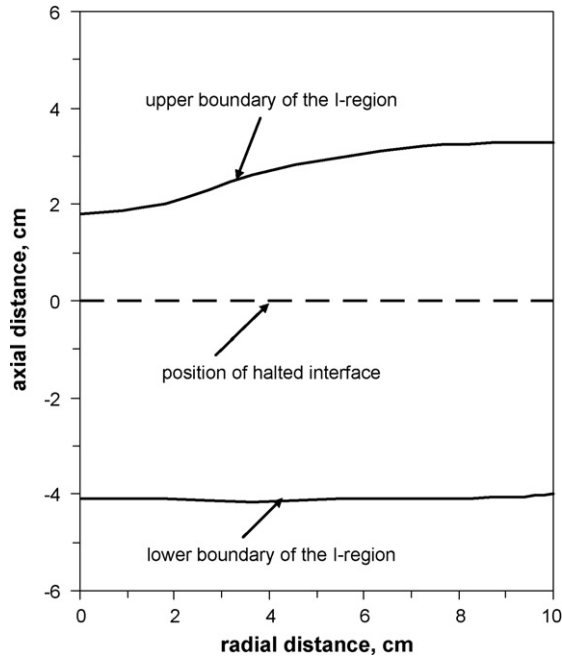
$$\alpha = \frac{D\varepsilon}{kT_m^2} \quad (2)$$

For a long time it was not clear whether the drift coefficients  $\alpha_V$  (for V) and  $\alpha_I$  (for I) are large or negligible, in regard to their contribution into  $(V/G)_{cr}$ . Now we have realized that some published data provide a strong evidence in favour of an essential uphill drift of both point defects. We discuss this piece of evidence and present the results of simulation designed to reproduce the reported data, and to deduce the drift coefficients (and accordingly the drift energies). The drift coefficients turn out to be similarly high both for V and I.

## 2. Evidence of a strong defect drift

This evidence is provided by reported microdefect patterns in CZ silicon crystals grown in the vacancy mode – at  $V/G > (V/G)_{cr}$  – with a temporary halt [2–4], typically of 2 h. During the halt, the pull rate was either zero [2,3] or very low [4], which corresponds to an extreme case of the I-mode. Accordingly, a near-interface crystal region, some centimetres deep, becomes dominated by self-interstitials that in-diffuse from the crystal–melt interface. This effect is basically due to a higher diffusivity of I, in comparison to V. In crystals quenched immediately after the halt [2] this in-diffused I-region – well separated from the main V-region in the crystal bulk – could be delineated by copper decoration. By transmission electron microscopy of as-grown samples, small intrinsic dislocation loops (I-agglomerates) were found in the I-region. This halt/quench experiment does not tell anything about a possible defect drift but

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**Fig. 1.** Schematic image of the microdefect pattern found [3] in a V-type crystal grown with a temporary 2 h halt. The halt-induced I-region is confined between the two boundaries that separate it from the two V-type crystal portions, one located above the upper boundary (in the crystal part grown before the halt) and the other below the lower boundary (in the part grown after the halt).

it is important to confirm the existence of a halt-induced I-region located close to the halted interface.

In some works [3,4] the halt was followed by a resumed growth – at the same pull rate  $V$  used before the halt – and thus again in the V-mode. In the completed crystal, an I-region was found—located around the once-halted interface. Importantly, it was wider than that found after halt-and-quench. Clearly, during resumed growth, the I-region expands by diffusion of self-interstitials, at the expense of the two surrounding V-regions, one located in the old (previously grown) crystal portion, and the other in the new portion grown after the halt.

Beside this natural expansion, there is a striking effect of a strong downward shift of the I-region, into the new crystal portion. For instance, the reported I-region [3] (surrounded by two large V-regions) has a lower edge at 4 cm below the halted interface, and the upper edge at 2–3 cm above the interface, as illustrated schematically in Fig. 1. This phenomenon is clear evidence in favour of an uphill drift of point defects. Without a drift, the I-region would reside predominantly within the old crystal part (above the halted interface), only slightly propagating into the new part. This expectation was fully confirmed by simulations.

In principle, a drift of only vacancies could account for the shift of the I-region into the new crystal portion: the vacancies in the new crystal portion (a lower portion in Fig. 1) drift downward clearing the space for the self-interstitials that fill this space by diffusion. At the same time, the downward vacancy drift in the old crystal portion will partially annihilate the I-region and thus push the upper V/I boundary downward.

### 3. Point defect parameters

The point defect parameters required for reliable simulation of the whole growth process (preliminary growth stage that leads to steady-state defect profiles, then halt, and finally resumed growth) were deduced [5] from various sources. First, the transport capaci-

ties  $P_I(T)$  and  $P_V(T)$  (the products of the diffusivity and equilibrium concentration) were deduced from Au and Zn diffusion and self-diffusion:

$$P_I = D_I C_{Ie} = (6.69 \times 10^{26} \text{ cm}^{-1} \text{ s}^{-1}) \exp\left(\frac{-5.15 \text{ eV}}{kT}\right) \quad (3)$$

$$P_V = D_V C_{Ve} = (4.8 \times 10^{23} \text{ cm}^{-1} \text{ s}^{-1}) \exp\left(\frac{-4.33 \text{ eV}}{kT}\right) \quad (4)$$

Next, the melting-point difference of the two equilibrium concentrations,  $C_{VI} = C_{Ve} - C_{Ie}$ , is specified approximately ( $\approx 1.6 \times 10^{14} \text{ cm}^{-3}$ ) by the total volume of voids monitored by laser scattering tomography [6].

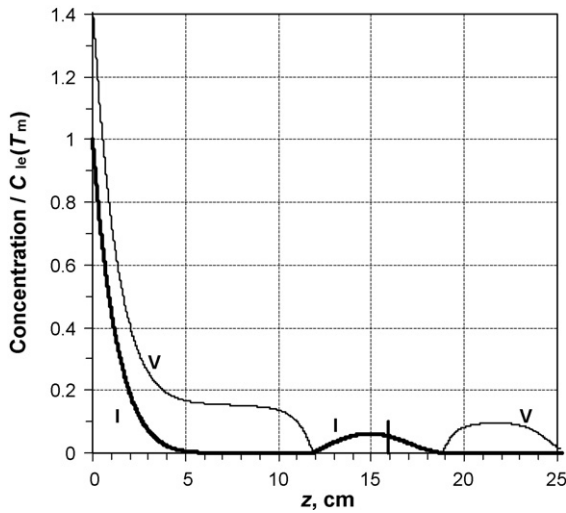
The vacancy diffusivity  $D_V$  was deduced [5] from the vacancy profiles installed into wafers by rapid thermal annealing; the resulting value was  $1.7 \times 10^{-4} \text{ cm}^2/\text{s}$  at  $1240^\circ\text{C}$ . A recent refined analysis (to be published elsewhere) – including not only out-diffusion of V but also a loss of vacancies by the formation of non-detectable complexes with oxygen – gives a somewhat smaller value, close to  $10^{-4} \text{ cm}^2/\text{s}$ . In the present work, we adopt this updated value. The migration energy of V is close to 0.38 eV [5]; this energy follows from the just mentioned value of  $D_V$  at high  $T$  ( $1240^\circ\text{C}$ ) and the diffusivity values at very low  $T$  deduced from radiation experiments [7]. The diffusivity  $D_V$  extrapolated to  $T_m$  is equal to  $1.37 \times 10^{-4} \text{ cm}^2/\text{s}$ . All the parameters at  $T_m$  are specified: the vacancy equilibrium concentration  $C_{Ve}$  is expressed as  $P_V/D_V = 4.55 \times 10^{14} \text{ cm}^{-3}$ , the self-interstitial equilibrium concentration  $C_{Ie}$  is equal to  $C_{Ve} - C_{VI} = 2.95 \times 10^{14} \text{ cm}^{-3}$ , and  $D_I = P_I/C_{Ie} = 9.25 \times 10^{-4} \text{ cm}^2/\text{s}$ . For  $D_I$  we tentatively adopt a low activation energy 0.2 eV—considering a high absolute value of  $D_I$ ; the results are actually insensitive to the adopted energy provided it is low ( $<0.4 \text{ eV}$ ). The activation energies for the concentrations follow from Eqs. (3) and (4): 4.95 eV for  $C_{Ie}$  and 3.95 eV for  $C_{Ve}$ .

The I–V recombination is assumed to be fast—maintaining the equilibrium value of the product of two actual concentrations,  $C_V C_I$ .

There remain only two unknown parameters: the drift coefficients  $\alpha_V$  and  $\alpha_I$ , to be determined in the present work.

### 4. Simulation procedure and results

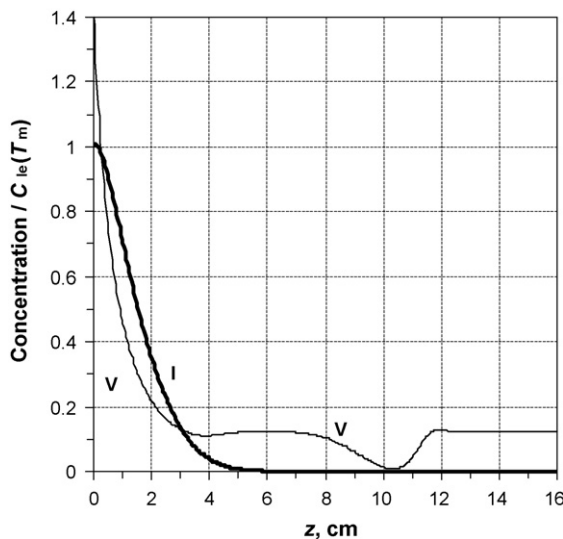
Axial profiles of V and I were calculated in a 1D approximation—taking into account only axial transport of the defects. The temperature profile is assumed to be linear in  $z$ , and thus characterized by only one parameter,  $G$ . According to Ref. [3],  $G$  is close to 4 K/mm, while the growth rate (before and after the halt) is  $V = 1.3 \text{ mm/min}$ . The diffusion equations (including the defect transfer at the total velocity of  $V - \alpha_V G$  for V, and  $V - \alpha_I G$  for I) were solved in order to trace the evolution of the axial defect profiles in the course of the whole growth process. In these simulations, it is also important to take into account the vacancy agglomeration into voids that occurs at some distance from the interface, because the vacancy loss to voids reduces the amount of vacancies that arrive by drift to the upper I/V boundary of the I-region and push this boundary down. The agglomeration was described by a “lumped model” [8] based on the replacement of the actual averaged void radius  $\langle R \rangle$  with a square root of  $\langle R^2 \rangle$ ; in this way the agglomeration process is decoupled from the size distribution of voids and reduced to local processes: void nucleation, evolution of  $\langle R^2 \rangle$  and reduction in  $C_V$ . The vacancy transport is suppressed not only by a vacancy loss to voids but also by the formation of immobile complexes with oxygen [9], VO and VO<sub>2</sub>. A conventional “binding temperature” of  $1050^\circ\text{C}$  was adopted; it separates a higher- $T$  range (where free vacancies dominate) from a lower- $T$  range (where VO<sub>2</sub> are the dominant vacancy species). The stage of resumed growth was traced until the temperature at the once-halted



**Fig. 2.** Computed axial profiles of vacancies (V) and self-interstitials (I) in a crystal grown with a temporary halt of 2 h. The resumed growth lasts until the temperature at the once-halted interface (buried deep within the crystal body and marked by the vertical bar, at  $z = 16$  cm) reaches  $950^\circ\text{C}$ . The positions of the lower edge of the I-region (4 cm below the halted interface) and of the upper edge (3 cm above) correspond to the location of the I-region actually found and shown schematically in Fig. 1.

interface reached  $950^\circ\text{C}$ . At lower  $T$ , the interstitial transport will be suppressed both by the formation of I-agglomerates [6] and by replacing the self-interstitials with carbon interstitials [9].

Various values for the drift coefficients  $\alpha_V$  and  $\alpha_I$  were tried. The actual positions of the two edges of the I-region (4 cm below the once-halted interface, and 2–3 cm above the interface—see Fig. 1) were reproduced by simulation only within very narrow intervals of the drift coefficients—practically for unique values of these coefficients. The proper value of  $\alpha_V$  is close to  $1.6 \times 10^{-5} \text{ cm}^2/(\text{s K})$  ( $0.096 \text{ mm}^2/(\text{min K})$ ), and  $\alpha_I$  is almost the same ( $1.65 \times 10^{-5} \text{ cm}^2/(\text{s K})$ ). The computed profiles are shown in Fig. 2; the thin line refers to the total vacancy concentration including the vacancies agglomerated into voids and those trapped by oxygen



**Fig. 3.** Computed V-profile (thin line) and I-profile (thick line) developed in a crystal first grown in the V-mode and then halted for 2 h. The I-dominated region, with the upper edge at  $z = 3$  cm (the distance from the halted interface) is formed due to the halt.

into VO and VO<sub>2</sub>. The thick line shows the self-interstitial concentration.

The profiles developed by the end of the halt period (right before the crystal is either quenched or further grown) are also interesting because these could be fixed by quenching [2] allowing for a comparison of actual and simulated profiles. The simulated profiles are shown in Fig. 3. There is a relatively wide I-region; the upper edge (the right one in Fig. 3) is close to that found experimentally [2]. The lower edge of the I-region (the left one in Fig. 3) is located close to the interface; a narrow band adjacent to the interface is V-dominated, since the interfacial concentration  $C_{Ve}$  is higher than  $C_{le}$ . A vacancy depression at about  $z = 10.5$  cm is caused by the vacancy diffusion to voids located to the right, at  $z > 11.5$  cm, and also by a vacancy drift to the left, away from the voids. This region of vacancy depression is also seen in Fig. 2, at  $z \approx 25$  cm.

## 5. Discussion

The deduced values for the drift coefficients imply a relatively fast drift: for the actual gradient of  $G = 4 \text{ K/mm}$ , the drift velocity is  $0.38 \text{ mm/min}$  (for both V and I). It is smaller than the pull rate  $V$  but comparable to it. With both the drift coefficients and the diffusivities known, the drift energies are calculated by Eq. (2):  $\varepsilon_V = 29 \text{ eV}$ ,  $\varepsilon_I = 4.5 \text{ eV}$ . The drift is considered weak if the drift energy is much smaller than the average defect formation energy  $E = (E_V + E_I)/2 \approx 4.5 \text{ eV}$ , otherwise the drift is strong. From this point of view, the self-interstitial drift is strong while the vacancy drift can be considered as gigantic:  $\varepsilon_V$  is much larger than  $E$ .

The critical ratio  $(V/G)_{cr}$  can be calculated using the expression [1] through the point defect parameters taken at  $T_m$ :

$$\left(\frac{V}{G}\right)_{cr} = \left(\frac{E}{kT_m^2}\right) \left(\frac{P_I - P_V}{C_{VI}}\right) + \left(\frac{\alpha_V C_{Ve} - \alpha_I C_{le}}{C_{VI}}\right) \quad (5)$$

The first term in the right-hand part is a contribution due to the defect diffusion, and the second term—due to the drift. The former is 0.14 (in the units of  $\text{mm}^2/(\text{min K})$ ) while the latter is 0.095. The total computed critical ratio is then 0.235. This number is a bit outside the usually accepted reasonable range,  $0.12\text{--}0.20 \text{ mm}^2/(\text{min K})$ , for the scattered values of  $(V/G)_{cr}$  deduced directly from the observed transition between the V-mode and the I-mode of growth. One reason for the discrepancy (and for the scatter) is inaccuracy in the value of  $G$  normally obtained by a global heat transport simulation that assumes some simplified description of the melt flow and relies on the thermal properties of Si (solid and liquid) and of the furnace materials that are not known precisely.

The main conclusion of this work is that the drift of point defects (in the uphill direction) is so strong that it cannot be ignored in any simulation of the real crystal growth process, designed to reproduce reliably the actual microdefect pattern. On the other hand, in wafer processing (when a temperature difference between the two wafer surfaces is not large) the drift of point defects is of essentially no importance.

## References

- [1] V.V. Voronkov, R. Falster, J. Appl. Phys. 86 (1999) 5975–5982.
- [2] M. Okui, T. Tanaka, T. Kanda, T. Ono, K. Egashira, S. Kuragaki, Proceedings of Kazusa Academy Park Forum on the Science and Technology of Silicon Materials, 1997, pp. 444–449.
- [3] K. Nakai, H. Yokota, J. Takahashi, A. Tachikawa, K. Kitahara, A. Ikari, M. Tanaka, in: H. Yamada-Kaneta, K. Sumino (Eds.), The Forum on Science and Technology of Silicon Materials, Hawaii, Japan Technical Information Service, Tokyo, 2001, pp. 73–86.

- [4] T. Iwasaki, Y. Tsumori, K. Nakai, H. Haga, in: H.R. Huff, W. Bergholz, K. Sumino (Eds.), *Semiconductor Silicon*, Electrochemical Society, Pennington, NJ, 1994, pp. 744–757.
- [5] V.V. Voronkov, R. Falster, *Mater. Sci. Eng. B* 134 (2006) 227–232.
- [6] T. Saishoi, K. Nakamura, H. Nakajima, T. Yokoyama, F. Ishikawa, J. Tomioka, in: C.L. Claeys, P. Rai-Choudhary, M. Watanabe, P. Stallhofer, H.J. Dawson (Eds.), *High Purity Silicon V*, ECS Proceedings, vol. 98-13, Electrochemical Society, Pennington, NJ, 1998, pp. 28–40.
- [7] G.D. Watkins, *J. Phys. Soc. Jpn.* 18 (Suppl. II) (1963) 22–30.
- [8] M.S. Kulkarni, V.V. Voronkov, *J. Electrochem. Soc.* 152 (2005) G781–G786.
- [9] V.V. Voronkov, R. Falster, *J. Electrochem. Soc.* 149 (2002) G167–G174.