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Impacts of thermal stress and doping on intrinsic point defect properties and clustering during single crystal silicon and germanium growth from a melt

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ABSTRACT

This paper reviews recent considerable progress made in the last few years in understanding the behavior and properties of intrinsic point defects close to moving melt/solid Si interfaces during single crystal Si growth from a melt. The so called Voronkov criterion allows to determine whether the grown Si crystal is interstitial *I*- or vacancy *V*-rich. This criterion is written as the ratio Γ of the pulling rate v over the thermal gradient G at the interface. Crystals pulled with Γ above a critical value Γ_{crit} are vacancy-rich while below Γ_{crit}, they are interstitial-rich. Various expressions based on the intrinsic point defect thermal equilibrium concentration and diffusivity have been proposed to calculate Γ_{crit} and are briefly discussed in this paper. Recently it was shown that the thermal stress at the interface and heavy doping with neutral and/or electrically active impurities, have a considerable impact on the intrinsic point defect balance and thus also on Γ_{crit}. Furthermore, high energy barriers of formation energies of *I* and *V* around three or four atom layers from (001) free surface support a model in which the boundary conditions of the point defect concentrations at the surface in simulations can be set at fixed values. The situation is quite different for Ge single crystal pulling where the vacancy is always the dominant intrinsic point defect so that the Voronkov criterion cannot be applied. Prediction of vacancy cluster concentration/size distributions as a function of the pulling conditions is however still possible. The possibility of reaching Voronkov criterion conditions for Ge by doping with specific impurities is also discussed. Finally, impacts of stress and doping on self-diffusion in Si and Ge are evaluated with comparing the previous experimental results.

1. Introduction

This paper reviews recent considerable progress made in the last few years in understanding the behavior of intrinsic point defects close to moving melt/solid silicon interfaces. The so called Voronkov criterion decides whether silicon crystallized from a melt is interstitial *I*- or vacancy *V*-rich. This criterion is written as the ratio Γ of the pulling rate v and the thermal gradient G at the melt/solid interface. Crystals pulled with Γ above a critical value Γ_{crit} are vacancy-rich while below Γ_{crit}, they are interstitial-rich. It was recently shown that:

- thermal stress at the interface which was neglected so far, has a considerable impact on the intrinsic point defect balance and should therefore be taken into account when calculating Γ_{crit} or solving the intrinsic point defect transport equations [1–9];
- heavy doping both with neutral and/or electrically active impurities, has an important impact on Γ_{crit} and the experimentally observed effects on grown-in point defect cluster type and distribution can be reproduced quantitatively based on ab initio calculations [4,9–11];
- high energy barriers of *I* and *V* around three or four atomic layers from (001) free surface support a model in which the boundary conditions of the point defect concentrations at the surface in simulations can be set at fixed values [12].

The situation is quite different for Ge single crystal pulling where the vacancy is always the dominant intinsic point defect so that the Voronkov criterion [13] cannot be applied. This paper also reviews recent understandings of intinsic point defect properties in Ge crystals.

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Table 1
Physical properties of intrinsic point defects used for modeling point defect distribution and clustering during Cz crystal growth. In the last two columns, the corresponding Γ_{crit} values are listed calculated with Eqs. (1) and (4).

Ref.	D_V	H_V^m	C_V^{eq}	H_V^f	D_I	H_I^m	C_I^{eq}	H_I^f	Γ_{crit} with (1)	Γ_{crit} with (4)
	$\left(\frac{10^{-4}cm^2}{s}\right)$	(eV)	$\left(\frac{10^{14}}{cm^3}\right)$	(eV)	$\left(\frac{10^{-4}cm^2}{s}\right)$	(eV)	$\left(\frac{10^{14}}{cm^3}\right)$	(eV)	$\left(\frac{mm^2}{Kmin}\right)$	$\left(\frac{mm^2}{Kmin}\right)$
[18–20]	0.3388	0.457	8.649	3.7	3.749	0.937	7.031	4	0.1365	0.1432
[21,22]	0.3990	0.4	8.307	4	3.978	0.9	6.822	4	0.1572	0.1572
[21,22]	1.463	0.38	5.804	4.12	5.073	0.3	4.719	4.35	0.1477	0.1561
[23,24]	0.631	0.4	4.58	3.84	7.656	1.18	3.174	3.77	0.1419	0.1403
[4]	0.5421	0.45	6.510	3.88	0.8898	0.88	6.397	3.68	0.1773	0.1573

Finally, impacts of stress and doping on self-diffusion in Si and Ge are evaluated with comparing the previous experimental results.

2. The Voronkov criterion for intrinsic point defect cluster free single crystal growth

2.1. The original voronkov equation of 1982

As early as 1982, Voronkov proposed an equation to calculate Γ_{crit} based on the thermal equilibrium concentration and diffusivity of the intrinsic point defects in Si [13,14]:

$$\Gamma_{crit} = \left[\frac{v}{G}\right]_{crit} \approx \frac{(C_I^{eq} D_I - C_V^{eq} D_V) H_{av}^f}{(C_V - C_I) k_B (T_m)^2},$$

with

$$H_{av}^f = \frac{H_I^f + H_V^f}{2}. \quad (1)$$

C^{eq} and D are the intrinsic point defect thermal equilibrium concentration and diffusivity, respectively, both at melting temperature T_m. H^f is the intrinsic point defect formation enthalpy and C the actual intrinsic point defect concentration at the melt/solid interface in most cases assumed to be the bulk thermal equilibrium concentration. k_B is the Boltzmann constant.

2.2. The "improved" voronkov equation of 2009

A more sophisticated expression was proposed more than 25 years later [15]:

$$\Gamma_{crit} \approx \frac{(C_I^{eq} D_I - C_V^{eq} D_V) H_{av}^f}{(C_V - C_I) k_B (T_m)^2} + \frac{\alpha_V C_V^{eq} - \alpha_I C_I^{eq}}{C_V - C_I}, \quad (2)$$

with the second term at the right hand side due to intrinsic point defect drift and α_V and α_I the vacancy and self-interstitial drift coefficients.

Eq. (2) can also be written as [6]

$$\Gamma_{crit} \approx \frac{C_I^{eq} D_I (H_{av}^f + Q_I) - C_V^{eq} D_V (H_{av}^f + Q_V)}{(C_V - C_I) k_B (T_m)^2}. \quad (3)$$

Q is the reduced heat of transfer, or simply the heat of transfer of V or I. Note that Q has an opposite sign to α.

2.3. A new derivation of the basic expression for Γ_{crit}

An alternative basic expression for Γ_{crit} comparable to (1) was derived recently in a straightforward way as [1,2]

$$\Gamma_{crit} \approx \frac{C_I^{eq} D_I H_I^f - C_V^{eq} D_V H_V^f}{(C_V - C_I) k_B (T_m)^2}. \quad (4)$$

A very important contribution to this theory was also provided by Sinno et al. [16,17], where a first experimental validation of Voronkov's criterion expressed as Eq. (4) was provided, together with a mathematical justification of this formula by means of an asymptotic expansion technique.

Eqs. (1)–(4) lead to similar predictions although the set of intrinsic point defect properties leading to a best match between the calculated and experimentally determined Γ_{crit} values will differ. Hereby it should be noted that the experimental value of Γ_{crit} will depend on the accuracy with which G is calculated. The equations also indicate that cast silicon crystals (v=0) are always I-rich while very fast pulled silicon crystals will always be V-rich.

2.4. Working without the voronkov criterion?

The Voronkov criterion was developed at a time when computer resources were scarce and was very useful as $[v/G]_{crit}$ can more or less be estimated and applied experimentally. Nowadays it is however no longer a problem to solve numerically the differential equations describing intrinsic point defect transport and recombination taking into account also the curved melt/solid interface.

The sets of intrinsic point defect parameters obtained in the literature are summarized in Eqs. (1) and (4) (Table 1) [18–24], or in Eqs. (2) and (3) (Table 2) [6,15]. In these tables, H^m is the intrinsic point defect migration enthalpy.

Regarding Eqs. (1) and (4), Frewen et al. used an approach of global parameterization of multiple point defect dynamics models in Si [18–20] combining crystal growth data on the shape and position of the boundary between V-rich and I-rich crystal parts with intrinsic point defect properties extracted from Zn diffusion experiments [25,26]. This enabled the authors to obtain a single set of intrinsic point defect parameters (listed at the top in Table 1) allowing them to explain both sets of experimental data. Also references to the work of Kulkarni [21,22], Nishimoto et al. [23,24], and Vanhellemont et al. [4] are added in Table 1. Similar to Frewen et al. [18–20], Nishimoto et al. [23,24] and also Nakamura et al. [26], constrained the range of the extracted parameters by imposing that $D(T_m)C^{eq}(T_m)$ and $H^f + H^m$ are in agree-

Table 2
Intrinsic point defect parameters determined using Eqs. (2) and (3).

C_V^{eq} (10^{14} cm^{-3})	H_V^f (eV)	D_V (10^{-4} cm^2)	Q_V (eV)	C_I^{eq} (10^{14} cm^{-3})	H_I^f (eV)	D_I (10^{-4} cm^2)	Q_I (eV)	Γ_{crit} with (3) (mm^{2}K^{-1}min^{-1})	Ref.
6.49	3.94	0.445	0	4.84	4.05	5.00	1.01	0.1627	[6]
4.55	3.95	1.37	−29	2.95	4.95	9.25	−4.5	0.2322	[15]