Two-dimensional model of the intrinsic point defects behaviour during Cz silicon crystals growth

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ABSTRACT

Two-dimensional mathematical model of the intrinsic point defects recombination during Cz growth of dislocation-free silicon single crystals is developed. The results of its verification are compared with the data of the one-dimensional model supposing the "fast" vacancies and interstitials recombination near the liquid-solid interface. For various growth conditions and with using of the calculated two-dimensional temperature fields in Cz silicon crystals the resulting distributions of these intrinsic point defects in a crystal are analyzed.

Keywords: two-dimensional (2D) model; Czochralski (Cz) crystal growth, calculation; silicon; intrinsic point defects (IPD); vacancy; interstitial; recombination.

1. INTRODUCTION

Diffusive and convective transport of the intrinsic point defects (IPD) and its recombination in a growing crystal near a liquid-solid interface (LSI) causes the main influence on peculiarity of a defect formation in dislocation-free silicon single crystals (formation of voids and oxygen particles, congestions of interstitials)[1,2]. At present the model of the defect formation in dislocation-free single crystals working effectively is based on the one-dimensional approximation supposing the "fast" IPD recombination and using transformation of two basic transfer equations to one equation by replacement of variables[2].

However in the two-dimensional case it is more reasonable to solve the initial system of two equations, applying the standard Newton algorithm linearizing two equations with the subsequent approximation and the numerical solution by the finite elements method[3]. In addition there is a possibility of calculation in regions with curved boundaries by taking into account the curved LSI shape and by using the temperature and temperature gradients distributions calculated by using the global thermal Cz model[4]. In given work this approach was developed.

For verification of the two-dimensional algorithm the case of the one-dimensional (given analytically) temperature field in a crystal was applied, because in this case the concentration of IPD fields are known on basis of the one-dimensional modeling[2,5]. The input parameters influence on the residual vacancies and interstitials concentrations and on the recombination threshold are investigated. In particular ξ_{crit} value is studied according to the known transition criterion from the "interstitials" growth mode to the "vacancy" one (here $\xi = V_p/G$ and V_p is the pulling rate, G is the axial temperature gradient at LSI). The further calculations are carried out for a two-dimensional temperature field, appropriate to growing of silicon single crystals of 150 mm in diameter. Two-dimensional fields of the IPD concentrations are calculated at various growth stages (30, 50 and 80% of length of the cylindrical grown crystal part) and for various pull rates.

2. FORMULATION OF THE PROBLEM

The crystals growth from a melt by Cz method is carried out in the high-temperature hot zone, which thermal efficiency depends on a design of thermal shields and properties of chosen thermoinsulating materials. Besides, hot zone should satisfy technological conditions of perfect crystal growth. In ref [4] the conjugate mathematical model for the investigation of heat transfer processes in hot zone for the Cz method was developed. In the radiative-conductive approximation temperature fields and the distribution of G for consecutive growth stages of silicon single crystals of 150 mm in diameter were

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investigated. Calculations of heat transfer processes were carried out for 10 consecutive growth stages depending on volume of a cylindrical part of a growing crystal (in percentage): the beginning of a cylindrical part, then the stages corresponding to the increase of crystal volume on every 10%. The regularities of axial temperature gradients and ξ values change at the LSI were obtained which can be used for theoretical estimations of the IPD recombination processes in silicon. In fig. 1 the frame of a hot zone and isotherms are shown for the 50%-s crystal growing stage.
During Cz silicon crystal growth the vacancies and interstitials transfer is realized by the convective diffusion. We neglect

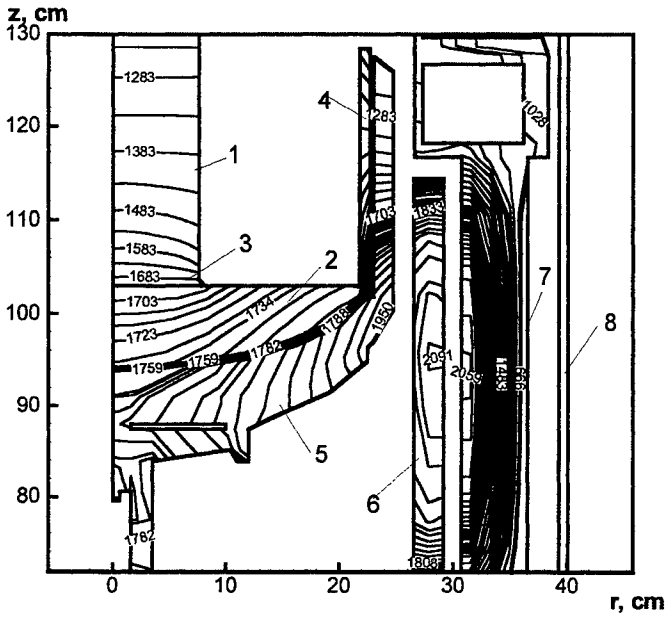

Fig.1. Temperature distribution in the hot zone for the 50%-s crystal growing stage: 1 – single crystal, 2 – melt, 3 – liquid-solid interface, 4 – crucible, 5 – susceptor, 6 – resistive heater, 7 – thermal shields, 8 – water-cooled tank.

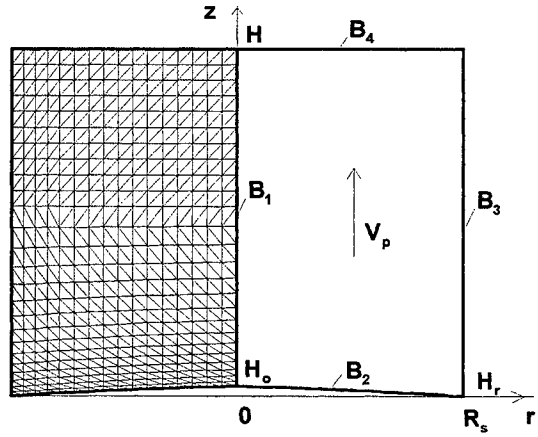

Fig.2. Scheme of the calculation region (on the right) and according mesh of 6-nodes triangular finite elements (on the left).
Here: B_1 - symmetry axis, B_2 - LSI, B_3 is crystal surface, B_4 is top boundary of a recombination.

the thermodiffusion. The stationary equations system for calculation of the vacancies $C_v(r,z)$ and interstitials $C_i(r,z)$ concentrations has the following form:

$$V_p \frac{\partial C_v}{\partial z} = \mathrm{div}(D_v \nabla C_v) - \omega \qquad (1),$$

$$V_p \frac{\partial C_i}{\partial z} = \mathrm{div}(D_i \nabla C_i) - \omega \qquad (2)$$

Coefficients of diffusions (D_v, D_i) and equilibrium concentrations of vacancies and interstitials (C_{ve}, C_{ie}) are set by using its values (C_{vm}, C_{im}) at the melting temperature (T_m) as follows:

$$D_v(T) = D_{vm}\exp(-E_{vD}/kT + E_{vD}/kT_m),\ D_i(T) = D_{im}\exp(-E_{iD}/kT + E_{iD}/kT_m),$$
$$C_{ve}(T) = C_{vm}\exp(-E_v/kT + E_v/kT_m),\ C_{ie}(T) = C_{im}\exp(-E_i/kT + E_i/kT_m)$$

Here $\omega = K_{vi}(C_vC_i - C_{ve}C_{ie})$, the recombination factor $K_{vi} = A_{vi}(D_v + D_i)\exp(-E_{rec}/kT)$ and $A_{vi} = 4\pi r_{cap}$ (r_{cap} - radius and E_{rec} - recombination energy); E_{vD}, E_{iD} - energies of vacancies and interstitials diffusion activation, and E_v, E_i -

energies of vacancies and interstitials equilibrium activation. In these formulas the constants are used: silicon melting temperature $T_m = 1683K$ and Boltzman constant $k = 8.625\times10^{-5}$ eV/K.

The experimental value of a transition - ξ_{crit} =0.132 mm^2/Kmin from vacancies to interstitials growth mode corresponds to the following parameters[5]:

$$D_{vm} = 4.0\times10^{-5}\,\text{cm}^2/s,\ E_{vD} = 0.35\ \text{eV},\ D_{im} = 5.25\times10^{-4}\,\text{cm}^2/s,\ E_{iD} = 0.20\ \text{eV}; \qquad (3)$$

$$C_{vm} = 7.2\times10^{14}\ \text{cm}^{-3},\ E_v = 4.5\ \text{eV},\ C_{im} = 5.2\times10^{14}\,\text{cm}^{-3},\ E_i = 4.6\ \text{eV}.$$

The value of recombination energy barrier E_{rec} is not known. At its choice the satisfaction to "fast" recombination condition is required. This condition is satisfied, if E_{rec} = 1.5 eV is set. Radius of recombination r_{cap} is equal to 3.0 x 10^{-8} cm.

The scheme of calculation region is given on Fig. 2. Accordingly boundary conditions are set as follows:

$$\frac{\partial C^{(i)}}{\partial n} = 0 \ \text{ at } B_1, B_4 \text{ boundaries}, \quad C^{(i)} = C_e^{(i)} \text{ at } B_2, B_3 \text{ boundaries}.$$

Here $C^{(i)}$ corresponds to the actual values of C_v, C_i and $C_e^{(i)}$ are appropriate equilibrium concentrations. For calculations a geometry and sizes of a recombination region were chosen as following values: H = 115.2 cm and $H_r = H_o$ = 103.7 cm, according to the size of global thermal Cz model.

The stationary equations (1) - (2) are solved iteratavely by a finite element method (FEM) in the Galerkin's formulation. The approximation of unknown concentrations C_v and C_i is represented as decomposition on square-law basic functions on 6-nodes triangular elements (fig. 2). Preliminary a residual for each equation is linearizated by Newton's method. FEM equations system is solved by a frontal method. As a whole the algorithm of the solution of the discrete FEM equations, earlier developed for global thermal model is kept[4].

3. COMPARISON WITH ONE-DIMENSIONAL MODEL

For the test based on the data of one-dimensional recombination model the temperature field in a crystal was set as only depending upon z:

$$\frac{1}{T(z)} = \frac{1}{T_m} + \frac{G\cdot z}{T_m^2},$$

and at a lateral crystal surface the boundary condition was set as follows: $\frac{\partial C^{(i)}}{\partial n} = 0$.

Here G is axial gradient of temperature at LSI. In this case calculation results on based of 2D-model should correspond to one-dimensional data[2,5].

The comparison of V_p/G critical value at G changes in range of 30-300 K/cm and at V_p pull rate variation near (v-i) - transition threshold shows, that the transition occurs at constant value of $(V_p/G)_{crit}$ = 0.132 mm^2/Kmin, that precisely corresponds to the data[5].

In a case of 2D model a value of K_{vi} at T_m was equal $\approx 2\times10^{-19}$ cm^3/s and for this value a "fast" recombination condition of $C_{ve}C_{ie} = C_vC_i$ is satisfied with rather high accuracy. Also a value of a residual C_{vs} concentration for a vacancies mode (G = 120 K/cm, V_p = 1.61 mm/min) was equal to $C_{vs} = 3.9\times10^{12}$ cm^{-3}. According to ref [5] this value is a little lower: $C_{vs} = 2.8\times10^{12}$ cm^{-3}. The small divergence can be caused by distinction in approximation of the basic equations, because in ref [2,5] the "fast" recombination condition is used for transformation of (1) - (2) system to one equation. Opposite, in given 2D- model the initial (1)-(2) system is solved and the "fast" recombination condition follows from the calculations.

Thus, it is possible to consider, that for an one-dimensional temperature field the received results rather well correspond to 1D-data.

4. IPD BEHAVIOUR IN TWO-DIMENSIONAL THERMAL FIELD

In a case of 2D thermal field the boundary C_v, C_i concentrations are set as $C_v = C_{ve}$ and $C_i = C_{ie}$ at a lateral crystal surface. Input 2D thermal fields are set according to results of calculations by a global thermal model[4] for different crystal growth stages. In this case the radial inhomogeneities of an axial temperature gradient G at LSI plays the important role. Therefore determining its are two values of ξ: $\xi_o = V_p/G_o$ - at an axis and $\xi_R = V_p/G_R$ - at a lateral crystal surface. Its ratio with ξ_{crit} determines the recombination results and a growth mode: vacancy (v), interstitials (i) or mixed (v-i). For the latter case

a so-called OSF-ring is created in a crystal[3]. Radius of this ring is determined experimentally and this characteristic plays an important role at IPD distribution verification.

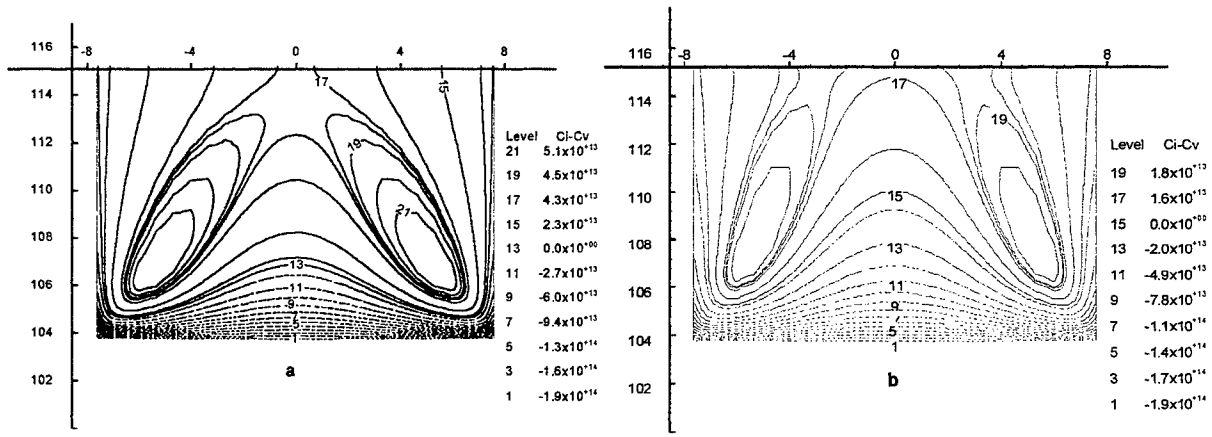

Fig.3. Isolines of the IPD concentration difference ($C = C_i - C_v$ [cm^{-3}]) for various crystal growth stages at the interstitial growth mode: a - 30% body, V_p = 0.39 mm/min; b - 50%, V_p = 0.37 mm/min.

According to (3) the parameters of 2D model correspond to ξ_{crit} = 0.132 mm^2/Kmin. However for 2D thermal field a value of ξ_{crit} requires an additional check. For this purpose the appropriate parametrical calculations were carried out, in which the pull rate V_p and values of temperature gradients (G_o and G_R) were varied at various crystal growth stages. In a number of calculations (50- and 80%-s' growth stages) the value of ξ_{crit} was checked by means of V_p change for conditions according to an identical temperature field in a crystal, i.e. without the appropriate recalculation of a thermal field on global thermal model.

For 30% and 50% growth stages the appropriate values V_p = 0.39 and 0.37 mm/min and the axial temperature gradients are 35 and 30 K/cm at an axis, 51 and 42 K/cm at a crystal edge. At 30 % stage: ξ_o = 0.111, ξ_R = 0.077, and at 50 %: ξ_o = 0.126, ξ_R = 0.088 mm^2/Kmin, i.e. at B_4 boundary is realized the interstitials mode (fig. 3a,b), because $\xi < \xi_{crit}$.

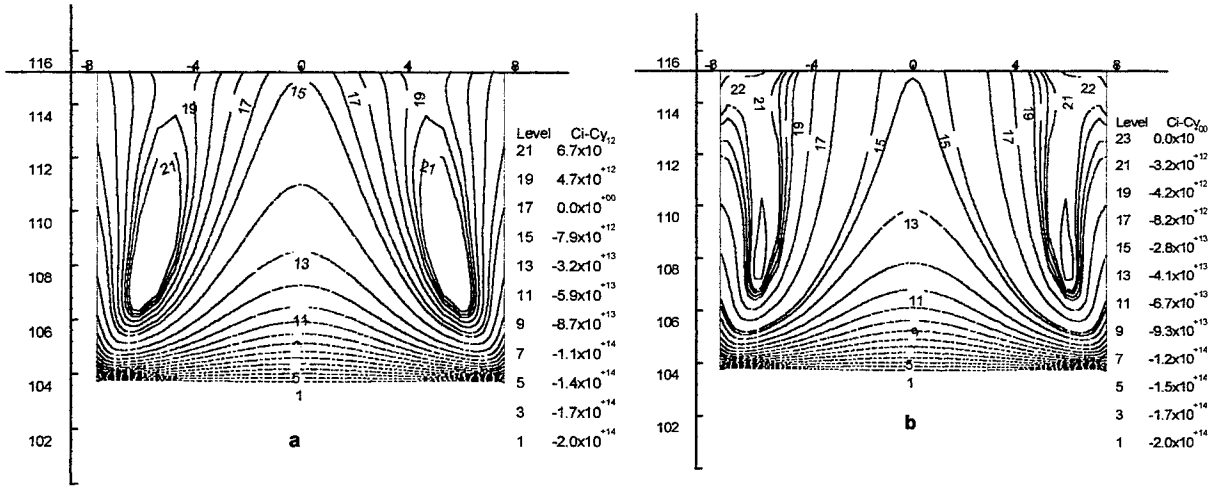

Fig.4. Isolines of the IPD concentration difference for the 50%-s growing stage and pull rates according to the mixed (*v-i*) and vacancy (*v*) growth modes: a - V_p = 0.42 mm/min; b - 0.47 mm/min.

All calculations were carried out at the initial conditions according to equilibrium concentration values of vacancies and interstitials in calculation region. For the chosen parameters (3) the equilibrium vacancies concentration exceed the equilibrium interstitials concentration. Therefore for initial iterations the prevalence of vacancies concentration is observed. For the subsequent iterations an action of the interstitials source in a region of the greatest temperature gradients (near LSI and a crystal edge) leads to a visible effect. It results in characteristic elliptical shapes of concentration isolines $C = C_i - C_v$. On fig. 4a,b the vacancies and interstitials distributions are shown at pull rates, which are a little larger, than in the previous case for the 50%-s growth stage: $V_p = 0.42$ and 0.47 mm/min. In this case thermal data corresponds to former value $V_p = 0.37$ mm/min, and the change of pull rate is taken into account only in the recombination equations (1)-(2).

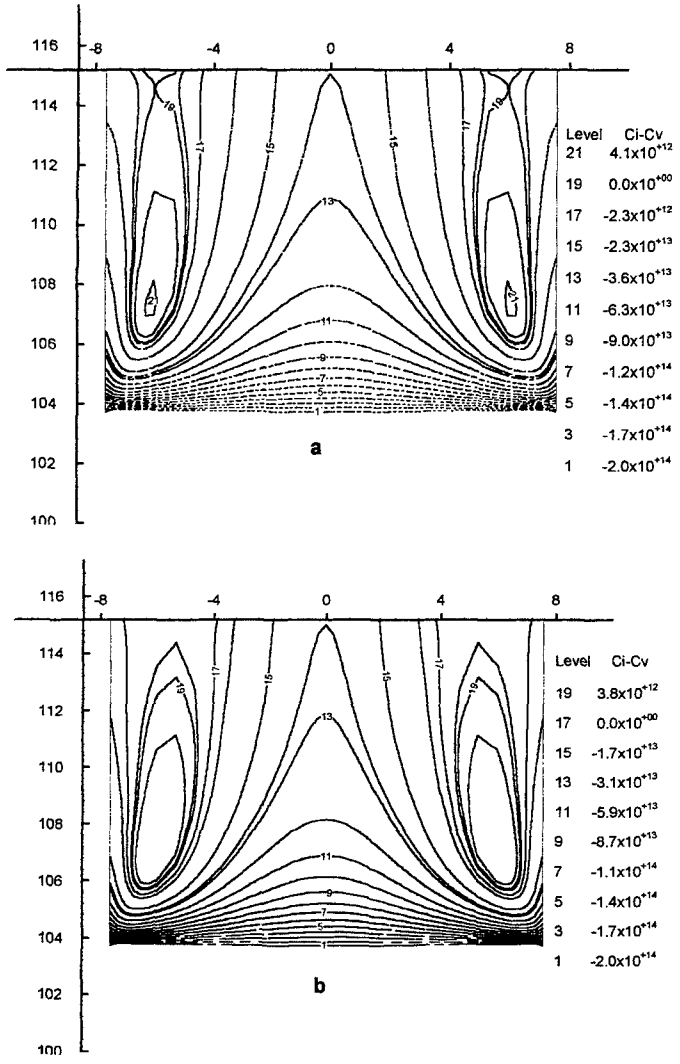

Fig.5. Isolines of the IPD concentration difference for various crystal growth stages at $V_p = 0.50$ mm/min corresponding to the following growth modes:
a - transition from the mixed (*v-i*) to the vacancy (*v*) mode at the 50%-s stage;
b - formation of the mixed (*v-i*) mode at the 80%-s stage.

The growth of V_p increases ξ: $\xi_o = 0.143$, $\xi_R = 0.100$ and $\xi_o = 0.159$, $\xi_R = 0.112$ mm^2/Kmin, accordingly. In particular at Vp = 0.42 mm/min is created a mixed v-i mode, which turns into a vacancies mode at increasing of pull rate till 0.47 mm/min. Let's notice, that ξ_R remains smaller than ξ_{crit}.
Strictly speaking, a pull rate change causes the changes of a temperature field in a crystal. These changes my be accounted for 50% growth stage at $V_p = 0.50$ mm/min. The axial temperature gradient increases then to 32 K/cm et the center and to 46 K/cm at the crystal edge. It gives next values: $\xi_o = 0.159$ and $\xi_R = 0.110$ mm^2/Kmin. The interstitials region extends essentially such that the vacancies distribution is divided from a top boundary (fig. 5a).

Similar changes occur at increase of pull rate for the 80%-s growth stage. At V_p = 0.35 mm/min the appropriate axial gradients at the axis and at the crystal edge are equal G_o = 22 and G_R = 48 K/cm, and ξ_o = 0.110 and ξ_R = 0.073 mm^2/Kmin. It may be a confirmation of an interstitials growth mode.
However at larger pull rate - Vp = 0.50 mm/min, the values ξ grow so that there is mixed v-i mode (ξ_o = 0.157, ξ_R = 0.104 mm^2/Kmin). Respective calculation results are shown in fig. 5b.
The main results of solution of this stationary recombination problem are the radial distribution of residual concentrations of vacancies C_v (r) and interstitials atoms C_i (r) at the top boundary of calculation region B_4 (Fig. 2). These data are necessary for further plotting of summarizing 2D distributions of residual IPD defects in the crystal (which are plotted on based of calculated data for 10 and more growth stages).
Here for comparison the radial output distributions C_v (r) and C_i (r) on the top boundary of recombination region are given in fig. 6 for the 50% growth stage and two pull rate values, according to interstitials (V_p = 0.37 mm/min) and mixed v-i (V_p = 0.50 mm/min) modes. The analysis of the graphs at r = 0 shows, that in the interstitial mode C_i exceeds C_v concentration essensially. The similar graphs for mixed (v-i) mode show significant growth of vacancies concentration and practically complete disappearance of interstitial atoms at the axis.

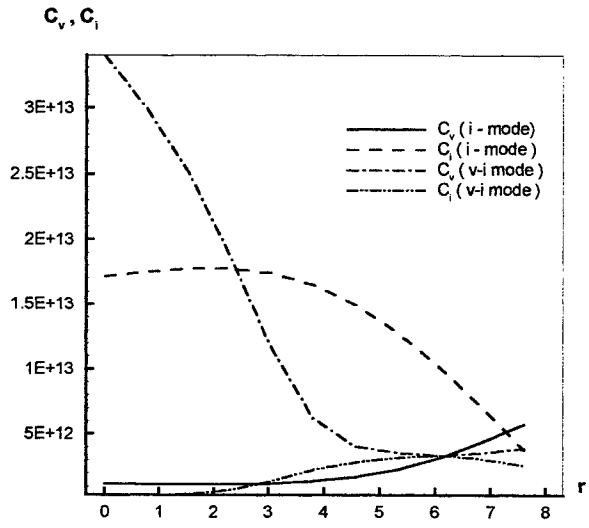

Fig.6. Radial distributions of C_v, and C_i concentrations on the top boundary (z = H) corresponding to pull rate variations at the 50%-s crystal growing stage. Here: the interstitial (i) mode is at V_p = 0.37 mm/min, and the mixed (*v-i*) mode arises at V_p = 0.50 mm/min.

5. CONCLUSIONS

Considered 2D model develops the previous 1D model of IPD behaviour near the LSI during Cz silicon crystal growth. The assumption of the "fast" vacancies and interstitials recombination taken into account at a choice of parameters by using of 1D data was confirmed numerically. The values of the residual IPD concentrations (after a recombination) were verified too.
Using 2D global thermal Cz model for calculations of 2D thermal growth history gives the possibility of IPD behaviour modeling adequately at various changes of thermal shields in a hot zone and for different pull rates. In particular this model gives possibility for investigation of important 2D effects such as OSF ring in dislocation-free silicon single crystals caused by radial temperature gradients.

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