Effect of rotation on impurity distribution in crystal growth by Bridgman method

A I Fedyushkin¹, N G Burago¹ and A A Puntus²

¹ Ishlinsky Institute for Problems in Mechanics of the Russian Academy of Sciences
² Moscow Aviation Institute (National Research University)

E-mail: fai@ipmnet.ru

Abstract. This work is devoted to the numerical (FE) study of the influence of crucible and submerged heater rotation on the distribution of doping gallium in germanium crystals grown by Bridgman method with submerged heater. The influence of crucible and submerged heater rotation on the impurity distribution in the melt and in the crystal for constant and oscillating rotation speeds is shown for the earth conditions and weightlessness conditions.

1. Introduction

The rotation of liquid and gas is widely used in many industrial plants, engines, turbines, heat-mass transfer devices, in medicine, in the food and chemical industries, in particular, in the technology of crystal growth. The first studies of the effect of rotation on the characteristics of heat and mass transfer in a liquid were based on semi-empirical correlations obtained from experiments and on the basis of some particular analytical solutions of the equations of fluid mechanics.

In the process of crystal growth, it is desirable to increase the rate of production of perfect crystals. To do this, it is necessary to organize the mode of convective mixing of the melt so that 1) heat from the growing crystal is removed as quickly as possible, 2) the solidification front is remained flat and 3) the impurity distribution is uniform over the crystal radius. In studies [1-2] for GdAlO3 crystal growth preference was given to the method of ACRT (accelerated crucible rotation technique), proposed in [2].

The effect of rotation on the thickness of the boundary layer on a rotating disk was investigated in [3] and it was shown that the thickness of the laminar boundary layer does not depend on the radius of the disk and is proportional to the speed of rotation to degree 1/2. The same dependence was used in [4] to determine the thickness of the boundary layer at the crystallization front in the case of crystal rotation.

Examples of controlling the melt mixing by gravity, rotation, and vibrations are given in [5]. The authors of [6] give an overview of the results of crystal growth under rotational-oscillatory (ACRT) and vibration effects on the melt flow in order to control growth. In [7], the results of mathematical modeling of the effect of vibration effects on heat and mass transfer during crystal growth are presented.

When growing single crystals by the Bridgman vertical method, the crucible rotation is used to symmetrize the temperature field, reduce the temperature gradients orthogonal to the gravity vector and reduce convection. The rotation of the crucible and the bodies immersed in the melt can also significantly affect the distribution of impurities in the melt, since the alloying impurities for semiconductors, as a rule, have Schmidt numbers much greater than 1 (the ratio of diffusion and kinematic viscosity coefficients).

In this paper, we consider the modeling of heat and mass transfer for the vertical Bridgman method with a submerged heater [8]. The immersed heater in the Bridgman method separates the melt region
and allows controlling convective mixing near the crystallization front. A review of this method is presented in [9].

Simulation of non-stationary processes of heat and mass transfer require large time resources and computing power, but the development of computational methods and computers currently allows such calculations. Reviews on the results of mathematical modeling of heat and mass transfer during crystal growth and the prospects for the development of these works are given in [10-11].

In [12], for the Bridgman method with a submerged heater, the influence of the rotation of the submerged heater on the shape of the crystallization front of a NaNO₃ crystal was experimentally and numerically studied and numerical and experimental data were compared.

This work is devoted to the numerical (FE) study of the influence of crucible and submerged heater rotations on the distribution of doping gallium in germanium crystals for space and Earth conditions grown by vertical Bridgman method with submerged heater.

2. Mathematical model
The melt unsteady flow is assumed two-dimensional axisymmetric and described by Navier-Stokes equations for an incompressible viscous fluid in Boussinesq approximation.

\[
div \mathbf{U} = 0,  \tag{1}
\]

\[
\rho_0 \frac{du}{dt} = -\frac{\partial p}{\partial r} + \mu \left( \Delta u - u/r \right),  \tag{2}
\]

\[
\rho_0 \frac{dv}{dt} + \frac{\rho_0 \rho g}{r} = \mu \left( \Delta v - v/r^2 \right),  \tag{3}
\]

\[
\rho_0 \frac{dw}{dt} = -\frac{\partial p}{\partial z} + \mu \Delta w - \rho_0 g \beta T,  \tag{4}
\]

\[
dT/dt = k_\mathcal{T} \Delta T,  \tag{5}
\]

\[
dC/dt = k_\mathcal{C} \Delta C,  \tag{6}
\]

where \( d/dt = \frac{\partial}{\partial t} + u \frac{\partial}{\partial r} + w \frac{\partial}{\partial z} \) and traditional notation is used.

Fig. 1 shows the solution domain, where \( R = 3.36 \text{cm} \) is the radius of the crucible, \( \delta = 0.1 \text{cm} \) is the size of the gap (3), \( h = 0.8 \text{cm} \) is the distance between submerged heater and growing crystal, \( S_{\text{sh}} \) is the submerged heater subdomain (1). It is assumed that the front of crystallization (5) is flat, crystal growth rate \( W = 1 \text{cm/hour} \) is constant and \( T_m = 937^\circ \text{C} \) is the melting point of germanium, \( C \) is concentration of gallium impurity. Sticking conditions are used on solid walls, \( \Omega_{cr} \) is the rotation rate of crucible (surface of crystal (5) and vertical walls of crucible), \( \Omega_s \) is rotation rate of submerged heater (1), \( \mu, k_\mathcal{T}, k_\mathcal{C} \) are coefficients of viscosity, heat conduction and diffusion, \( \beta \) is buoyancy coefficient, \( g \) is gravity acceleration.

Boundary conditions are taken as:

\[
r = 0, \ 0 \leq z \leq H : \ u = 0, \ v = 0, \ \partial w/\partial r = 0, \ \partial T/\partial r = 0, \ \partial C/\partial r = 0;  \tag{7}
\]

\[
0 \leq r \leq R, \ z = 0 : \ u = 0, \ v = 0, \ w = -W, \ T = T_m, \ k_\mathcal{T} \partial C/\partial z = W_z C (1 - k_0);  \tag{8}
\]

\[
r = R, \ 0 \leq z \leq h : \ u = 0, \ v = 0, \ w = 2\pi R \Omega_c, \ \partial T/\partial r = 0, \ \partial C/\partial r = 0;  \tag{9}
\]

\[
r = R, \ h < z \leq H : \ u = 0, \ v = 2\pi R \Omega_c, \ w = 0, \ T = T_{cr}(z), \ \partial C/\partial r = 0;  \tag{10}
\]

\[
(r, z) \in S_{\text{sh}} : \ u = 0, \ v = 2\pi R \Omega_s, \ w = 0, \ T = T_{cr}(r, z), \ \partial C/\partial n = 0;  \tag{11}
\]

\[
0 \leq r \leq R, \ z = H : \ u = 0, \ \partial v/\partial z = 0, \ \partial w/\partial z = 0, \ T = T_z, \ C = C_0;  \tag{12}
\]

Initial conditions are:
\[ t = 0, \quad 0 \leq r \leq R, \quad 0 \leq z \leq h : \quad u = 0, \quad v = 0, \quad w = -W_s, \quad T = T_m, \quad C = C_{01} \]  

\[ t = 0, \quad 0 \leq r \leq R, \quad h < z \leq H : \quad u = 0, \quad v = 0, \quad w = -W_s, \quad T = T_m, \quad C = C_{02} \]

At the front of crystallization we use third kind mass transfer condition (8) that accounts the crystal growth rate \( W_s \) and equilibrium segregation coefficient \( k_0 \).

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**Figure 1.** The scheme of growing crystals by the vertical Bridgman method with a submerged heater (a) and the scheme of the computational domain in a 2D axisymmetric mathematical model (b).

### 3. Numerical method

Consider the solution algorithm using the example of a typical convection-diffusion equation

\[
\frac{\partial A}{\partial t} + \mathbf{u} \cdot \nabla A = \nabla \cdot (k \nabla A) + \mathbf{F}
\]  

The solution was obtained with the help of the Galerkin-Petrov variation scheme [13]

\[
\int_V \left( \frac{A^{n+1} - A^n}{\Delta t^n} + \mathbf{u}^n \cdot \nabla A^{n+1} \right) (\delta A + \Delta t^n \mathbf{u}^n \cdot \nabla \delta A) dV + \int_V \tilde{\kappa}^* \nabla A^{n+1} \cdot \nabla \delta A dV = \int_V F^{n+1} \cdot \delta A dV + \int_{S \subset t \Delta t} P_{i}^{n+1} \cdot \delta A dS
\]

which is complemented by the main boundary conditions: \( t \geq 0, \quad \mathbf{r} \in S \): \( \mathbf{A}^{n+1} = \mathbf{A}_*(\mathbf{x},t^{n+1}) \) and initial conditions: \( t = 0, \quad \mathbf{r} \in V \): \( \mathbf{A}^0 = \mathbf{A}_i^0(\mathbf{x}) \). Values with asterisks are given. Natural boundary conditions: \( t \geq 0, \quad \mathbf{r} \in S \setminus S_d \): \( k \mathbf{n} \cdot \nabla \mathbf{A}^{n+1} = P_{i}^{n+1} = P_i(\mathbf{x},t^{n+1}) \) are taken into account in the written above Galerkin-Petrov variational equation. Values with asterisks are given. Value \( \tilde{\kappa}^* \) is the viscosity coefficient, corrected (decreased) by exponential fitting method [14] (in simplest form): \( \tilde{\kappa}^* = k^2 / (k + \mathbf{u}^n \cdot \mathbf{u}^n \Delta t^n) \).

The discretized problem was solved by a matrix-free iterative conjugate gradient method [15]. Each iteration is equivalent to calculating the time step using an explicit two-layer finite-difference scheme. The number of iterations to obtain a solution does not exceed the number \( \sqrt{N} \), where \( N \) is the number
of unknowns. Since the number of operations at each iteration is directly proportional to $N$, the number of operations at the time step is proportional to $N^{3/2}$. The required RAM is $5N$ (5 real arrays of length $N$).

Thus, the method used allows one to very quickly solve unsteady problems that require determining the behavior of hydrodynamic parameters over a long physical time. Note that although the formally implicit method is unconditionally stable, in order to obtain an acceptable calculation accuracy for convective flows, the time step in nonstationary problems must be limited by the Courant condition $\Delta t \leq \min_{k} \left( \frac{h_k}{(|u^k| + \varepsilon)} \right)$, $k=1,...,N$.

We also note that the equations of motion for the radial and axial velocities were solved together with the incompressibility condition, which was included in the variational equation as a constraint by the penalty function method. The value of the penalty coefficient was determined from the maximum modulus of velocity in the flow region so as not to increase the courant limit of the time step recorded above. Then the tasks for azimuthal speeds and temperature were solved separately.

4. Results

Figure 2 shows the effect of the rotation of the submerged heater on the germanium melt flow. Contour lines of flow function are depicted for two cases a) without rotation b) with rotation at a speed $\Omega_b = 0.3117 rps$.

![Figure 2. Flow function a) no rotation, b) rotation of submerged heater $\Omega_b = 0.3117 rps$.](image)

Fig. 2-4 show results of modeling. The effect of heater rotation on melt flow can be seen in Fig. 2 that shows flow function for two cases: without rotation (a) and with rotation of submerged heater (b). The influence of crucible and heater rotations on impurity distribution in grown crystal can be seen at Fig. 3-4.

![Figure 3. Isolines of impurity distribution in grown crystals without rotation of crucible and heater for terrestrial conditions (a) and for space conditions (b). Influence of heater rotation $\Omega_b = 0.05$ rps is presented for terrestrial conditions (c) and for space conditions (d).](image)
Figure 4. Isolines of impurity distribution in grown crystals with rotation of crucible and heater for terrestrial conditions: a) $\Omega_h = 0.05 \text{rps}, \Omega_c = 0.3117 \text{rps}$; b) $\Omega_h = -0.05 \text{rps}, \Omega_c = 0.3117 \text{rps}$; c–d) $\Omega_h = 0.05 \text{rps}$ and oscillatory rotation of heater with frequency 0.68Hz for two time instants $t=579 \text{sec}$ (c) and $t=816 \text{sec}$ (d).

Numerical results show that in terrestrial conditions the most homogeneous impurity distribution in grown crystals is observed in case of counter-rotating crucible and immersed heater (Fig. 4b). The effect of the harmonic oscillating rotation of the immersed heater was calculated with a frequency of 0.68 Hz. This effect is expressed in the appearance of additional wavy inhomogeneities in the distribution of the impurity in the melt and, as a result, in the grown crystal as it is seen in Fig. 4c-d.

Conclusions
A finite element modeling of hydrodynamics and heat and mass transfer was carried out for a model of the Bridgman method with a submerged heater for a long time, which made it possible to obtain impurity distributions in a crystal for different conditions and rotational speeds.

The results showed that the rotation of the immersed heater and crucible affect the distribution of impurities in the crystal. At certain rotational speeds, they can homogenize the distribution of impurities in the crystal, which suggests rotation as a way to control the distribution of impurities in the crystal.

Under zero gravity conditions, rotation can be a necessary alternative to natural convection for heat removal from a crystal, and at certain rotational speeds, as for terrestrial conditions, they can homogenize the radial distribution of impurities in a crystal.

The calculation results showed that the cyclically acceleration-slowdown rotation of the immersed heater is most effective for mixing impurities in the melt.

Analysis of the calculation results showed that for the optimal distribution of the impurity in the crystal, the rotational speed should be a function of time.

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