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DEVELOPMENT OF HORIZONTALLY ORIENTED CRYSTALLIZATION OF HIGH-MELTING DIELECTRIC SINGLE CRYSTALS

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Special features of mathematical heat- and mass-transfer models are considered; systems of equations that describe the height change for growing single crystals are determined, and recommendations are given according to which the single-crystal height is practically constant. Under conditions of ideal mixing of a melt, the dopant distribution in the crystal is given.

Crystals of high-melting oxides that are grown by the method of horizontally oriented crystallization (HOC) have a height that is variable along the length. We observe a substantial decrease in the height of the crystal in its trailing portion at a distance approximately equal to the length of the melt zone at the moment the entire initial material is melted. The variable height is explained by the dissimilar densities of the crystal and the melt, the dependence of the latter on temperature, and melt evaporation as well as the change in the length and average temperature of the melt in a boat. The larger the difference of the crystal and melt densities (the crystal density being higher than the melt density), the more nonuniform the height of the terminal portion of the crystal. The variable height leads to a decrease in the number of products manufactured from the crystal and makes its treatment more complicated.

The shaping of the height for a single crystal grown by the HOC method is affected by heat, mass-transfer, and diffusion processes in the crystal, melt, and initial material. This calls for the consideration of a mathematical model of heat- and mass-transfer processes in growing single crystals. We dwell on some special features of the development and use of these models to improve the process of growing single crystals and on the methods of practical realization of the growth of crystals.

As far as the physical character of the process is concerned, it is appropriate to separate the entire cycle of single-crystal production by the HOC method into the following periods: the preinitial period – there is a melt and the initial material in the boat (the temperature in the bow of the boat is higher than the phase-transition temperature); the first period – there is a crystal, a melt, and the initial material in the boat; the second period – there is a crystal and a melt in the boat; the third period – the initial step of crystal cooling. At the boundaries of the periods, we consider fixed states of the system: the beginning of boat travel, the initial state of the system when, in the bow of the boat, the melt temperature is equal to the crystallization temperature t_{cr}; the end of melting for the initial material and the end of melt crystallization. Figure 1 presents the periods of the cycle. When single crystals are grown by the HOC method, use is made of the following methods of practical realization of a growing cycle, which differ in the indicators: 1) loading of the boat with the initial material and dopants (a constant load or a load that is variable along the boat length); 2) the character of a variation in the heater capacity in crystal growing; 3) the direction of boat motion (foward and backward); 4) the velocity of boat motion (including the boat stop); 5) the character of feeding the boat with material.

At present, growing is usually effected when the height of the initial material is uniform along the boat length, the boat velocity is constant, and the heater capacity is constant or varying insignificantly [1, 2] (Fig. 2, curve ABFG).

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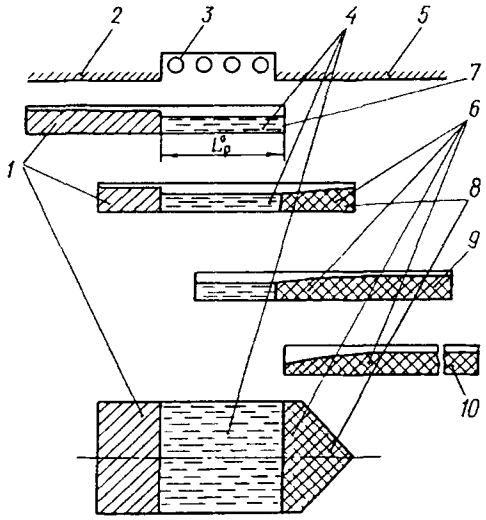

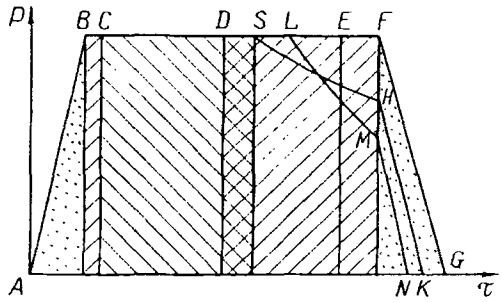

Fig. 1. Periods of the cycle of single-crystal growing by the method of horizontal-oriented crystallization: 1) initial material; 2) back crystallizer; 3) resistance heater; 4) melt; 5) front crystallizer; 6) crystal; 7) preinitial period; 8) first period; 9) second period; 10) third period.

Fig. 2. Change in the heater capacity in single-crystal growing: AB) melting of material in a boat and superheating of a melt before the beginning of boat motion; BC) preinitial period; CD) first period; DE) second period; EF) third period; FG, HK, MN) crystal cooling in the process of decreasing the heater capacity; SH) capacity decrease for a fixed position of a boat; LM) heater-capacity decrease when a boat travels in the direction opposite to the initial direction. P, kW; τ, h.

Of interest is the following method of realization of the growing cycle. The preinitial period and the first period, as well as a part of the second period of the cycle, are effected in the same manner as has been described above (Fig. 2, curve ABS). Once the end of the boat enters the heater zone for a distance and the maximum temperature is established in the melt near the end, the boat stops. The heater capacity begins to decrease at such a rate that the crystallization rate is approximately equal to the boat velocity. After the melt crystallization is completed (Fig. 2, point H), the heater capacity will continue to decrease with such an intensity as to ensure the prescribed rate of crystal cooling (Fig. 2, line HK). The process of decreasing capacity can be combined with the boat travel in the direction opposite to the initial direction (Fig. 2, curve LM). This permits a more intense decrease in the heater capacity. In the considered variants of the methods of realization of growth with the boat stop, the duration of the cycle is reduced, the electric-energy consumption decreases, and the in-service time for a heat assembly of the plant increases since the time of heater operation is reduced at high temperature. The productivity of the plant increases and the cost of the products decreases.

To analyze the process of shaping the height and concentration field of a single crystal, we must formulate a mathematical model of heat- and mass-transfer processes of growing single crystals from a melt by the HOC method. When developing it, we should allow for the following special features:

(1) the models are formulated for the periods of the cycle with allowance made for the methods of realization of the growing cycle;

(2) the process is considered in a multiphase conjugate system with the sought boundaries of phase transitions and exterior surfaces of the crystal and the melt;

(3) in connection with the low velocity of the boat and rate of melt crystallization (0.5–8 mm/h), the heat process in the system can be considered as quasistationary;

(4) the processes of heat transfer, dopant transfer in the melt, and shaping of the crystal height are interrelated and must be considered in combination.

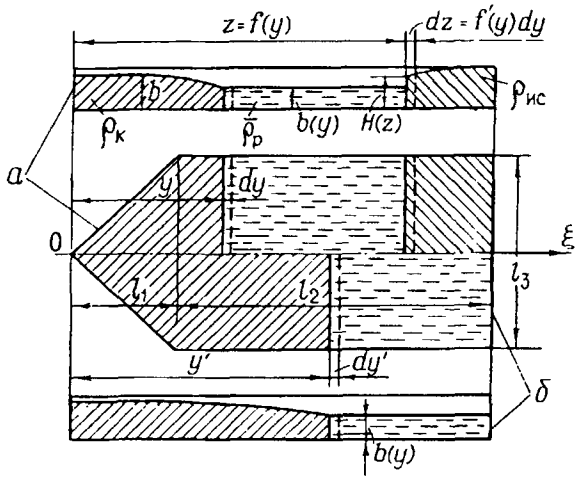

Fig. 3. Scheme for the formulation of the problem of shaping the height of a crystal and the dopant concentration in it: a, b) first and second periods of the cycle.

The latter special feature calls for incorporating into the mathematical model of heat- and mass-transfer processes the balance equations for the mass of the melt and dopants in it, the melt density as a function of temperature, and the crystallization temperature as a function of the dopant concentration at the boundary of the phase transition. Let us consider separately the problem of the shaping of the crystal's height and concentration field, taking the thermal conditions of growth to be known. The scheme for the formulation of the problem is presented in Fig. 3.

For the first period of the cycle, changes in the mass of the melt dM and the mass of the dopants in it dM', which have an effect on the height of the melt layer and dopant concentration in it, will be represented as follows:

$$dM = \left[(\rho_{in} H(z) - \rho_{m.cr} b(y)) l_3 f'(y) - (\rho_{cr} - \rho_{m.cr}) l_3(y) b(y) - \frac{F(y) V}{W}\right] dy, \quad (1)$$

$$dM' = \left[(\rho'_{in} H(z) - \rho'_m b(y)) l_3 f'(y) + \rho'_m \frac{\rho_{cr}}{\rho_{m.cr}} (1 - k) \rho'_p l_3(y) b(y)\right] dy. \quad (2)$$

The melt density as a function of temperature has the form

$$\rho_{mT} = \rho_{m.cr} [1 - \alpha (\overline{T} - T_{cr})]. \quad (3)$$

The height of the melt layer in the boat with allowance made for its density for different temperatures is determined by the expression

$$db = db^M + db^T; \quad db^M = \frac{dM}{\rho_{mT} F(y)}; \quad db^T = \frac{b}{Q} \frac{\partial Q}{\partial \rho} \frac{\partial \rho}{\partial T} \frac{\partial T}{\partial y} dy. \quad (4)$$

In view of (1) and (3), we represent expression (4) as follows:

$$db = \frac{1}{\varepsilon_3(y) F(y)} \times$$

$$\times \left\{H(z) l_3 f'(y) \varepsilon_2 - b(y) \left[l_3 f'(y) + l_3(y) \varepsilon_1 - \frac{\alpha \Phi'(y) \varepsilon_3(y) F(y)}{1 - \alpha \Phi(y)}\right] - \frac{VF(y)}{W \rho_{m.cr}}\right\} dy, \quad (5)$$

where $\varepsilon_1 = (\rho_{cr} - \rho_{m.cr})/\rho_{m.cr}$; $\varepsilon_2 = \rho_{in}/\rho_{m.cr}$; $\varepsilon_3(y) = \rho_{mT}/\rho_{m.cr}$; $\Phi = \overline{T} - T_{cr}$.

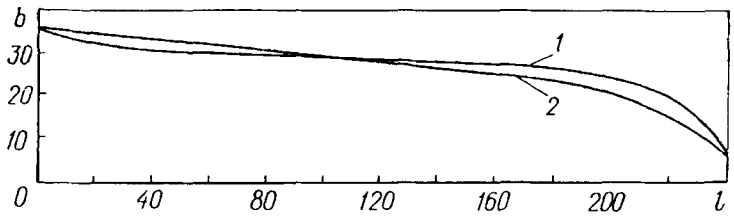

Fig. 4. Variation in the crystal height along the length: 1, 2) length of the melt zone (respectively, 0.05 and 0.1 m). b, l, mm.

Let us express the dopant concentration in the melt given its ideal mixing in the following manner:

$$\rho_{\text{m}}' = \rho_{\text{m}}' + \frac{dM'}{F(y)\, b(y)},$$

where y suggests that the quantity is taken for the position of the crystallization front y.

For the second period of the cycle, expressions (1), (2), and (5) will become

$$dM = \left[q - b(y)\, l_3 (\rho_{\text{cr}} - \rho_{\text{m.cr}}) - \frac{F(y)\, V}{W}\right] dy, \tag{6}$$

$$dM' = \left[q' - b(y)\, l_3\ (y)\,(1-k)\,\rho_{\text{m}}' \frac{\rho_{\text{cr}}}{\rho_{\text{m.cr}}}\right] dy, \tag{7}$$

$$db = \frac{1}{F(y)\,\varepsilon_3(y)} \times \left\{\frac{q}{\rho_{\text{m.cr}}} - b(y)\left[l_3(y)\,\varepsilon_1 - \frac{\alpha\Phi'(y)\,\varepsilon_3(y)\,F(y)}{1-\alpha\Phi(y)}\right] - \frac{VF(y)}{W\rho_{\text{m.cr}}}\right\} dy. \tag{8}$$

From the solution of Eqs. (5) and (8), we can obtain the height variation for the melt layer in the boat depending on the position of the crystallization front $y - b(y)$. The obtained value of $b(y)$ will determine the height variation for the crystal along its length y. To solve the problem, we need to formulate the initial condition:

$$\text{for}\quad y = 0 \quad b = b(0);\ \ z = z(0);\ \ \Phi = \Phi(0). \tag{9}$$

These quantities are found from the solution of the inverse problem of determining the initial state of the system. Calculations were performed under a specially prepared program. The length of the melt zone in the first period of the cycle was assumed to be constant. Figure 4 presents a variation in the crystal height for different lengths of the melt zone.

As the figure shows, for a smaller melt-zone length, the crystal has a more uniform height. The largest variation in the height occurs in the second period of the cycle because of the decrease in the length of the melt zone $l_1 + l_2 - y$.

We dwell on the production of a single crystal with height constant along the length. Let us assume that the average temperature of the melt in the process of crystal growth does not change:

$$\Phi'(y) = 0. \tag{10}$$

For the first period of the cycle, we will consider the melt-zone length L_{m} as constant. For $L_{\text{m}} = L_{\text{m0}} = \text{const}$, we have

$$f(y) = z = y + L_{\text{m0}};\ \ f'(y) = 1. \tag{11}$$

In the first period of the cycle, the constant height of the melt layer is obtained due to the variable-along-the-length loading of the boat with the initial material. Assuming $db = 0$ in (5), in view of (10) and (11) we obtain

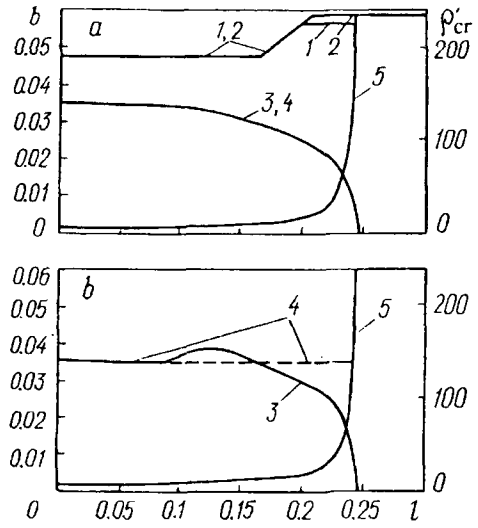

Fig. 5. Results of calculation of the height for a crystal and the dopant concentration in it: a) for a variable calculated load of the initial material; b) for a variable load and the action of mass sources; 1, 2) height of the initial-material load; 3. 4) crystal height; 5) dopant concentration in a crystal. b, l m; ρ'_{cr}, kg/m^3.

$$H(z) = \frac{1}{\varepsilon_3(y)\, l_3}\left(\frac{F(y)\, V}{W\rho_{m.cr}} + b(0)\,(l_3(y)\,\varepsilon_1 + l_3)\right). \tag{12}$$

In the second period of the cycle, a mass source of strength q is introduced to obtain a constant height. Assuming $db = 0$ in (8), in view of 10 we will have

$$q = l_3(y)\, b(0)\, \varepsilon_1 \rho_{m.cr} + \frac{VF(y)}{W}. \tag{13}$$

Under specially prepared programs, we calculated the crystal height for the case of its leveling on the initial section and along the entire crystal length. Figure 5a presents the load of the initial material that is calculated by formula (12) (curve 1) and a load that is larger than the calculated load (curve 2). As the figure shows, on the front section of the crystal of length $l_1 + l_2 - L_m$, the height is constant for the two variants of the load (curves 3 and 4). For the calculated load, on the back section of the crystal of length L_m, the height decreases substantially. In the case of the increased load, we observe a local increase in the crystal height, and the region with the substantial height decrease becomes smaller. This permits a larger yield of finished products from the grown crystal. In Fig. 5b, curve 4 characterizes the variation in the crystal height for the initial-material load, calculated by (12), and when the mass sources q are introduced in the second period of the cycle. The value of q was calculated by formula (13).

In this case, a practically constant crystal height is obtained. The mass sources can be introduced through feeding the boat with the melt from an independent source. Conditions (10) and (11) are satisfied by altering the heater capacity. The character of this alteration is determined experimentally or can be calculated under special programs developed on the basis of a general model of the heat- and mass-transfer process for the case of single-crystal growing by the HOC method.

As Fig. 5 shows, in the final step of crystal growth, there is a substantial increase in the concentration of dopants in the melt and the crystal whose control in the crystal can be effected by altering their load in the initial material along the boat length.

The statements of periodization and different methods of practical realization of the growing cycle, as well as special features of the development of mathematical models for heat- and mass-transfer processes, presented in this paper for the HOC method, can be used for analysis and improvement of single-crystal growing from a melt by other methods.

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NOTATION

ρ, density; W, crystallization rate; T, temperature; Φ, average excess temperature of the melt; k, equilibrium coefficient of distribution; α, temperature coefficient of melt density; V, rate of melt evaporation; H, height of the initial-material layer; b, height of the melt (crystal) layer; q, strength of the melt-mass source; q', strength of the dopant-mass source; F, melt surface; L, length of the melt zone; Q, melt volume; y, position of the crystallization front; z, position of the melting point for the initial material; M, melt mass; M', mass of dopants in the melt; $\overline{T}$, average temperature; ρ', dopant concentration; l_1, l_2, and l_3, boat sizes.

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