CRITERIA CHARACTERIZING THERMAL PROCESSES IN THE CRYSTALLIZATION OF THIN MELT LAYERS ON BACKINGS OF DIFFERENT MATERIALS

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We propose criteria to describe the thermal processes in the crystallization of thin melt layers on backings of different materials. We have established the relations between these criteria and their relationship to the conditions of crystallization.

The method of growing single crystals on backings of different materials (see, for example, [2-4]) involves the application of the semiconductor material (germanium, silicon) onto a backing in the form of an amorphous or polycrystalline film, which is then subjected to melting and subsequent crystallization as the melt cools. The crystallization process is accomplished in a vacuum. The heating of the specimen and the melting of the semiconductor material are accomplished by means of an electric heater which is placed underneath the backing, and the heat is removed through the outside surface of the melt by thermal radiation into the vacuum. References [5-9] are devoted to the development of the phenomenological theory of the process of growing single crystals.

In the one-dimensional approximation, assuming that the crystallization front is flat in shape and that it moves from the outside surface of the melt toward the backing* (Fig. 1), the process of melt crystallization is described by a nonlinear boundary problem of the form

$$\frac{\partial}{\partial x}\left[K(x)\frac{\partial\vartheta}{\partial x}\right] = c(x)\frac{\partial\vartheta}{\partial t},\quad -l<x<a, \tag{1a}$$

$$K(x)=\begin{cases}K', & y(t)<x\leqslant a\\ K, & 0<x<y(t),\\ K_1, & -l\leqslant x<0\end{cases}\qquad c(x)=\begin{cases}c', & y(t)<x\leqslant a\\ c, & 0<x<y(t),\\ c_1, & -l\leqslant x<0\end{cases} \tag{1b}$$

$$\left(\frac{\partial\vartheta}{\partial x}+h\vartheta\right)_{x=a} = -\frac{h}{4}, \tag{1c}$$

$$\vartheta(-l,\ t)=f(t), \tag{1d}$$

$$\vartheta[y(t),\ t]=0, \tag{1e}$$

$$k\left.\frac{\partial\vartheta}{\partial x}\right|_{x=y(t)+0} - \left.\frac{\partial\vartheta}{\partial x}\right|_{x=y(t)-0} = \alpha\frac{dy}{dt}, \tag{1f}$$

$$y(0)=y_0,\quad \vartheta(x,\ 0)=w(x). \tag{1g}$$

Here

$$\vartheta(x,\ t)=\frac{T(x,\ t)-T_c}{T_c},\quad h=\frac{4\varepsilon'\sigma T_c^3}{K'},\quad \alpha=\frac{Ld}{T_cK},\quad k=\frac{K'}{K}, \tag{1h}$$

*This is the preferable direction of the crystallization, since it reduces to the minimum the requirement imposed on the backing, and it is also possible to grow crystals at arbitrarily small rates of growth, needed to ensure structural integrity.

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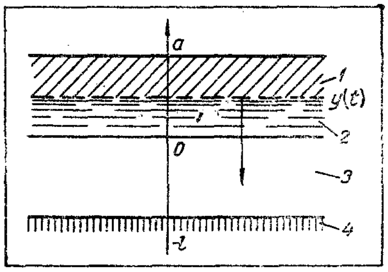

Fig. 1. Diagram showing the crystallization of a melt layer on a backing of a different material: 1) solid phase; 2) liquid phase; 3) backing; 4) heater; y(t) variable coordinate of boundary of phase separation.

and the initial temperature distribution is described by the function $w(x) = \lim \tilde{w}(x)$, where $\tilde{w}(x)$ is the solution of the steady-state problem of the form (1a, b, c) when $t = 0$, $c(x) = 0$, $y = y_0$, $\tilde{w}(y_0) = 0$. This corresponds to the initial value of the boundary-value function $f(0) = (kh/4)[a + (Kl/K_1)]$.

The boundary-value problem (1) represents a substantial complication of the familiar Stefan problem. To solve this problem for the case of relatively thin melt layers, $a/l \ll 1$, which is of the greatest practical significance, we have developed a method of successive approximations [6, 7] that is associated with the expansion of the unknown function in series of the parameter $\beta = cT_c/Ld$.

In the cases of practical importance, when 1) the lower surface of the backing is cooled in accordance with the linear law $f(t) = f(0) - \gamma t$, $\gamma = \text{const}$ and 2) at the instant $t = 0$ of the onset of crystallization the temperature of this surface instantaneously drops to some value $\vartheta_0 = \text{const}$, $\vartheta_0 - f(0) = D < 0$, and solution (1), in first approximation for β, can be presented by the following formulas, respectively:

$$\begin{aligned} &1)\quad u(\tau) \cong z_0 - \beta s \gamma \lambda \left\{ \frac{\tau^2}{2} - B_0 \tau + B_1 \left[1 - \exp\left(-\frac{\tau}{B_0} \right) \right] \right\}, \\ &2)\quad u(\tau) \cong z_0 + \beta s D \left\{ \tau - B_0 \left[1 - \exp\left(-\frac{\tau}{B_0} \right) \right] \right\}, \end{aligned} \tag{2}$$

where $u(\tau) = y(t)/l$; $\tau = t/\lambda$; $\lambda = a^2/\varkappa$; $\lambda_1 = l^2/\varkappa_1$; $z_0 = a/l$; $s = z_0^2/(\mu + z_0)$; $\mu = K/K_1$.

In the general case, the solution of (1) contains coefficients B_m of the form

$$B_m = \left(\frac{\lambda_1}{\lambda} \right)^{m+1} b_m, \quad m = 0, 1, 2, \ldots, \tag{3}$$

where

$$b_0 = \frac{\Phi_2(z_0)}{\Phi_0(z_0)}; \quad \Phi_0(z_0)\, b_m = (-1)^m \Phi_{2m+2}(z_0) + \sum_{i=1}^{m} (-1)^{i+1} b_{m-i} \Phi_{2i}(z_0), \quad m = 1, 2, \ldots,$$

while the integrals $\Phi_m(z)$, $z = x/l$ are determined by the recurrence relationships*

$$\Phi_{2n}(z) = \int_{-1}^{z} \Phi_{2n-1}(\zeta)\, d\Phi_0(\zeta), \quad \Phi_{2n-1}(z) = \int_{-1}^{z} \frac{c(\zeta)}{c_1} \Phi_{2n-2}(\zeta)\, d\zeta, \quad n = 1, 2, \ldots, \quad \Phi_0(z) = \begin{cases} 1 + z, & -1 \leqslant z \leqslant 0 \\ 1 + \dfrac{z}{\mu}, & 0 \leqslant z \leqslant z_0 \end{cases}.$$

* In the general case, solution (1) in first approximation has the form

$$u(\tau) = z_0 + \beta s \left[\int_0^{\tau} f_1(\tau)\, d\tau - \sum_{m=0}^{\infty} (-1)^m B_m \frac{d^{(m)} f_1}{d\tau^{(m)}} - \Omega(\tau) \right],$$

where $f_1(\tau) = f(\lambda\tau) - f(0)$, and the function $\Omega(\tau)$ satisfies the equation

$$\Omega(\tau) = -\frac{1}{\Phi_0(z_0)} \sum_{n=1}^{\infty} \left(\frac{\lambda_1}{\lambda} \right)^n \Phi_{2n}(z_0) \frac{d^{(n)} \Omega}{d\tau^{(n)}}$$

for the initial conditions

$$\left. \frac{d^{(n)} \Omega}{d\tau^{(n)}} \right|_{\tau=0} = \sum_{m=0}^{\infty} (-1)^{m+1} B_m \left. \frac{d^{(m+n)} f_1}{d\tau^{(m+n)}} \right|_{\tau=0}, \quad n = 0, 1, 2, \ldots$$

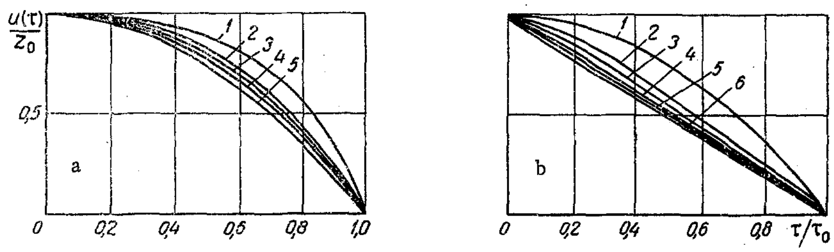

Fig. 2. Graphical representation of the motion of the crystallization front for various values of the criterion Z: a) cooling of the backing according to a linear law – 1) Z = 0.5; 2) 1; 3) 2; 4) 10; 5) ∞; b) instantaneous drop in the temperature of the lowest surface of the backing – 1) Z = 0.1; 2) 1; 3) 2; 4) 4; 5) 10; 6) ∞.

To characterize the thermal processes in the crystallization of a melt on a backing of a different material, let us introduce the following criterion into our examination:

$$Z = \frac{a}{V\lambda_1}, \tag{4}$$

which represents the ratio of the duration of the crystallization process to the relaxation time for the processes of thermal conductivity $\sim \omega_1$ [10] in the specimen. We can also impart the following form to formula (4):

$$Z = \frac{\lambda}{\lambda_1}\tau_0, \quad \tau_0 = \frac{t_0}{\lambda}. \tag{4'}$$

Because of the structure of (3) for the coefficients B_m the solutions of (1) can be presented in criterial form, thus making it possible to evaluate the role of the individual terms as a function of Z (when $Z \gg 1$ we have a quasisteady thermal regime, when $Z \sim 1$ the heat capacity of the media exerts significant influence on the progress of the thermal processes, and when $Z \ll 1$ the processes are particularly nonsteady in nature). In particular, from (2), (3), and (4') we have the following

$$1)\ \frac{u(\tau)}{z_0} = 1 - \frac{Z^2}{Y^{(1)^2}}\left\{\left(\frac{\tau}{\tau_0}\right)^2 - \frac{2b_0}{Z}\frac{\tau}{\tau_0} + \frac{2b_1}{Z^2}\left[1 - \exp\left(-\frac{Z}{b_0}\frac{\tau}{\tau_0}\right)\right]\right\},$$

$$2)\ \frac{u(\tau)}{z_0} = 1 - \frac{Z}{Y^{(2)}}\left\{\frac{\tau}{\tau_0} - \frac{b_0}{Z}\left[1 - \exp\left(-\frac{Z}{b_0}\frac{\tau}{\tau_0}\right)\right]\right\}, \tag{5}$$

where for the case of the cooling of the backing according to laws 1) and 2) we have introduced, respectively, the criteria

$$1)\ Y^{(1)^2} = \frac{2z_0}{\beta s\gamma\lambda}\left(\frac{\lambda}{\lambda_1}\right)^2 = \frac{2z_0(\mu + z_0)\alpha\varkappa_1}{\gamma\lambda_1},$$

$$2)\ Y^{(2)} = -\frac{z_0}{\beta s D}\frac{\lambda}{\lambda_1} = -\frac{z_0(\mu + z_0)\alpha\varkappa_1}{D}, \tag{6}$$

which are functions of the intensity of the cooling of the backing and of the parameters of the melt-backing system.

As follows directly from (5), the quasisteady regime $Z \to \infty$ is described by the first terms in the braces:

$$1)\ \frac{u(\tau)}{z_0} \approx 1 - \left(\frac{\tau}{\tau_0}\right)^2,$$

$$2)\ \frac{u(\tau)}{z_0} \approx 1 - \frac{\tau}{\tau_0}, \tag{6'}$$

while when $Z \ll 1$ the exponential terms play a predominant role.

Assuming in (5) that $\tau = \tau_0$ and ($u(\tau_0) = 0$) we find the relationship between the criteria Z and Y:

$$1)\quad Y^{(1)^2} = Z^2\left\{1 - \frac{2b_0}{Z} + \frac{2b_1}{Z^2}\left[1 - \exp\left(-\frac{Z}{b_0}\right)\right]\right\},$$
$$2)\quad Y^{(2)} = Z\left\{1 - \frac{b_0}{Z}\left[1 - \exp\left(-\frac{Z}{b_0}\right)\right]\right\}, \qquad (7)$$

and the criterion Y thus has the sense of the relative crystallization duration t_0/λ_1 in the quasisteady regime.

Because of (5) and (7), in the approximation being considered, the motion of the crystallization front is determined entirely by the magnitude of the criterion Z. Figure 2 shows the corresponding curves, plotted for various values of Z (these, and the examples presented later on, pertain to the case of the crystallization of layers of thin germanium melt, $z_0 \ll 1$, on sapphire backings with a thickness of $5 \cdot 10^{-4}$ m). The magnitude of Z also determines the duration $t_0 = \lambda_1 Z$ of the crystallization process and for a fixed value of the thickness of the melt layer, it determines the average rate of crystal growth, i.e., $\bar{V} = a/\lambda_1 Z$. Relationships (6) and (7) establish the agreement between Z, which determines the nature of the process, and the crystallization conditions – intensity of the cooling of the backing, and the parameters of the specimen.

Under the conditions of melt crystallization from its outside surface, the rate of crystal growth is bounded from above by the emittance of the melt being crystallized, $V < V_m = kh/4a$ (in the example under consideration, $V_m \simeq 3 \cdot 10^{-3}$ m/sec). Hence, in the light of (4), we find the lower bound for Z,

$$Z > Z_m,\quad Z_m = \frac{a}{V_m \lambda_1} = \frac{4 z_0 a \varkappa_1}{khl}, \qquad (8)$$

which also remains valid in the quasisteady regime. The values of the criteria $Y_m^{(1)}$ and $Y_m^{(2)}$, determined from (7), correspond to $Z = Z_m$, and because of (6), the maximum values for the cooling intensities are

$$1)\quad \gamma_m = \frac{1}{\lambda_1}\,\frac{2z_0(\mu + z_0)\,a\varkappa_1}{Z_m^2 - 2b_0 Z_m + 2b_1\left[1 - \exp\left(-\frac{Z_m}{b_0}\right)\right]},$$
$$2)\quad -D_m = \frac{z_0(\mu + z_0)\,a\varkappa_1}{Z_m - b_0\left[1 - \exp\left(-\frac{Z_m}{b_0}\right)\right]}. \qquad (9)$$

This makes it possible to present the relationships between Z and the cooling intensity – obtained from (6) and (7) – in dimensionless form

$$1)\quad \frac{\gamma_m}{\gamma} = \frac{Z^2 - 2b_0 Z + 2b_1\left[1 - \exp\left(-\frac{Z}{b_0}\right)\right]}{Z_m^2 - 2b_0 Z_m + 2b_1\left[1 - \exp\left(-\frac{Z_m}{b_0}\right)\right]},$$
$$2)\quad \frac{D_m}{D} = \frac{Z - b_0\left[1 - \exp\left(-\frac{Z}{b_0}\right)\right]}{Z_m - b_0\left[1 - \exp\left(-\frac{Z_m}{b_0}\right)\right]}. \qquad (10)$$

The family of curves $Z(\gamma_m/\gamma)$ and $Z(D_m/D)$, corresponding to the various values of the parameter z_0, are shown in Fig. 3.

When the cooling intensity for the backing exceeds the maximum values of (9), the temperature gradient at the boundary of separation between the melt and the backing may change sign and thermal conditions may arise that are suitable for the onset of melt crystallization from the side of the boundary with the backing before the crystallization which has started on the free surface is concluded. Once crystallization has started as well on the side of the backing, the possibility of single-crystal formation is excluded.

To establish the limits on the permissible cooling intensity for the backing, excluding the possibility of dual crystal formation from the thermal point of view, let us present (9) in the quasisteady approximation

TABLE 1. Critical Values of the Parameters for the Case of the Crystallization of Germanium Layers on a Sapphire Backing ($l = 5 \cdot 10^{-4}$ m)

z_0	Z_m	$Y_m^{(1)}$	$Y_m^{(2)}$	$\frac{-D_m}{f(0)}$	γ_m, sec^{-1}	$\frac{\gamma_p}{\gamma_m}$
0,1	10	9,85	9,85	1,02	$5,5\cdot 10^{-3}$	0,24
$4\cdot 10^{-2}$	4	3,85	3,85	1,04	$1,5\cdot 10^{-2}$	0,23
$2\cdot 10^{-2}$	2	1,85	1,85	1,09	$3,2\cdot 10^{-2}$	0,21
$1\cdot 10^{-2}$	1	0,83	0,83	1,20	$7,6\cdot 10^{-2}$	0,18
$3\cdot 10^{-3}$	0,3	0,15	0,15	1,90	$7,4\cdot 10^{-1}$	0,06

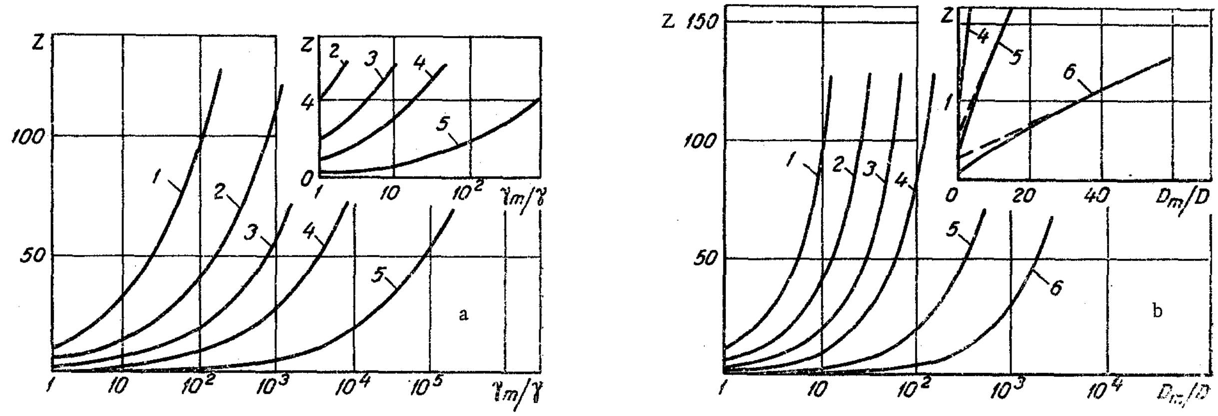

Fig. 3. Criterion Z as a function of the cooling intensity with a drop in the temperature of the lower surface of the backing, according to a linear law (a) and instantaneously (b): 1) $z_0 = 0.1$; 2) $4\cdot 10^{-2}$; 3) $2\cdot 10^{-2}$; 4) $1\cdot 10^{-2}$; 5) $3\cdot 10^{-3}$; 6) $1\cdot 10^{-3}$.

$$1)\quad \gamma_m^{(\mathrm{qu})} = \frac{2z_0(\mu + z_0)\alpha\varkappa_1}{\lambda_1 Z_m^2} = \frac{2f(0)V_m}{a},$$

$$2)\quad -D_m^{(\mathrm{qu})} = \frac{z_0(\mu + z_0)\alpha\varkappa_1}{Z_m} = f(0). \tag{9'}$$

It is clear that the limitation $-D < -D_m^{cb}$ (i.e., $\vartheta_0 > 0$ in this sense is sufficient in the cooling of the backing according to law 2), since it follows from this that $T > T_c$ in the region $-l \leq x < y(t)$. With cooling according to law 1), however, the condition $\gamma < \gamma_m^{cp}$ is insufficient, since the criterion Z includes the value of the average rate of crystal growth, whereas for the instantaneous values we have the limitation $V < V_m$. The sufficient condition for the permissible cooling intensity, $\gamma < \gamma_p$, in case 1) follows from the condition $f(\tau_0) > 0$, whence $f(0) = \gamma_p \lambda \tau_0 = \gamma_p \lambda_1 Y^{(1)}(\gamma_p)$ and $\gamma_p = \gamma_m^{cb}/4$.

The critical values of the parameters corresponding to a number of values for the thickness of the melt layer are given in Table 1.

The criteria introduced here can also be used to give the solution of (1) in criterial form, in successive approximations.

NOTATION

- T is the absolute temperature;
- T_c is the semiconductor crystallization temperature;
- ϑ is the dimensionless temperature;
- t is the time;
- x is the coordinate;
- $y(t)$ is a variable coordinate of the crystallization front;
- t_0 is the duration of the crystallization process;

$y(t_0) = 0$;

$f(t)$	is the dimensionless heater temperature;
a	is the thickness of the melt layer;
l	is the backing thickness;
K, c, $\varkappa$	are the coefficients of thermal conductivity, volume heat capacity, and thermal diffusivity for the liquid phase of the melt;
K', c', $\varkappa'$ and K_1, c_1, $\varkappa_1$	are the thermal coefficients for the solid phase and for the backing, respectively;
L	is the specific heat of semiconductor crystallization;
d	is its density;
ε'	is the solid-phase emissivity;
σ	is the Stefan constant;
V	is the rate of crystal growth;
$\bar{V}$	is the average value of the growth rate.

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*Reference No. 8 is missing in the original – Consultants Bureau.