

## Crystal Growth Mechanism in "Synthesis-solute-diffusion" Method in Ultrasonic Field

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Features crystal growth method "synthesis-solute-diffusion" when applied ultrasonic field are considered. Dependence of the crystal optical transmission heterogeneity frequency ultrasonic vibrations determined. System Tests showed that the optimal vibration frequency that provided a homogeneous crystals and permitting the maintenance of the solidification front in a predetermined position with an accuracy of  $\pm 5\%$  frequency is  $4 \text{ MHz} \pm 5$ . Comparison of the optimum frequency ultrasonic vibrations to increase uniformity in the mode of crystals convective transport under the Czochralski method and conditions of diffusive transfer method indicates a significant difference between these frequencies, i.e. character determines the transfer conditions of optimization process.

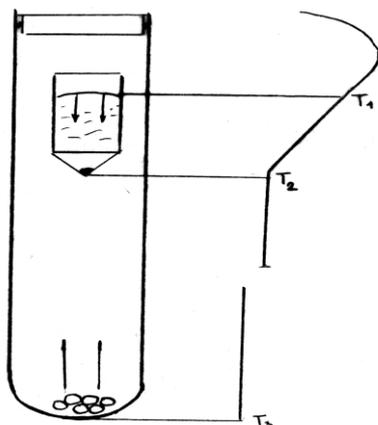
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### 1. INTRODUCTION

This method can be attributed to a group of directional solidification in the temperature gradient in the crystallization from solutions in molten metals. The advantage of this group of methods is the possibility to obtain crystals and films  $A^mB^n$  compounds at a relatively low temperature and pressure. This method was tested in the preparation of such compounds as single crystals of gallium and indium phosphide (partial pressure of phosphorus vapor at a temperature above the melting point of which is 60 and 30 atmospheres, respectively).

The essence of the method is as follows. In a sealed evacuated reactor (Fig. 1) is placed in a crucible loaded with a hitch member and the third group on the bottom of the crucible is placed hinge element of the fifth group



**Fig. 1** – Method of " synthesis- solution- diffusion". 1 - reactor, 2 - melt element of the fifth group, 3 - linkage element of the third group

### 2. EXPERIMENTAL

Reactor sealed in an oven set a temperature distribution in which the depth of the melt in the crucible is

created by a temperature gradient, and the fifth group element is maintained at a temperature at which its vapor pressure is greater than the dissociation pressure of the compound at a surface temperature of the melt. Evaporating element of the fifth group reacts at the surface of the melt in the crucible with the fifth group element and forms a compound film. This film is dissolved and the fifth group element is diffused into the lower portion of the crucible where the crystal growth begins. Growth rate is small, but the process takes place in conditions close to equilibrium, which ensures high quality and purity single crystals.

You can select the elementary stage of the process:

1. Evaporation of the fifth group element.
2. Reaction on the surface with the metal in crucible and form a compound film.
3. Dissolution of the film in the melt, diffusion of the fifth group element under the action of the temperature gradient.
4. Crystallization of the compound on the bottom of crucible.

The rate of dissolution of gallium arsenide gallium melt was first defined by [2].

The analysis of experimental data, that the dissolution rate in the system can be described by the law of Nernst:

$$\frac{\Delta m}{t} = V_{eff} \cdot S \cdot \Delta C \quad (1)$$

where  $V_{eff}$  – effective rate of dissolution,  $\Delta m$  – amount of undissolved material,  $\Delta C$  – the difference between the real and the liquidus concentration of the solute,  $t$  – dissolution time,  $s$  – the contact area of gallium and gallium arsenide.

Temperature dependence of the effective dissolution rate presented in a logarithmic scale, placed on a straight line, with an apparent activation energy of  $25.3 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$  for gallium arsenide. It confirms the exponential dependence of the effective dissolution rate

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from temperature. The obtained value of the activation energy coincided with the known data.

We have found that the diffusion rate can be determined based on the theory of non-stationary diffusion kinetics. It has been shown that the rate of diffusion depends on the time of the process and can be determined based on the theory of non-stationary diffusion kinetics. In the boundary conditions of limited source diffusion in semi-infinite space, the basic equation of unsteady diffusion kinetics has the form:

$$C = C_0 \left[ \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + \exp\left(\frac{k}{D}x + \frac{k^2}{D}t\right) \times \right. \right. \\ \left. \left. \times \operatorname{erfck}\left(\frac{t}{D} + \frac{x}{2\sqrt{Dt}}\right)\right) \right] \quad (2)$$

where  $k$  – rate constant of diffusion in the interpretation of Frank-Kamenetsky,  $C$  – concentration of the reactant.

Analysis of the equation (2) shows that the described process conditions:

1. Diffusion in the boundary of the melt flow equal to the macroscopic reaction rate and which can be found by differentiating the formula (2), is

$$J = kC_0 \exp\left[\frac{k^2}{D} \operatorname{erfck}\left(\sqrt{t/D}\right)\right] \quad (3)$$

The peculiarity of the problem is that the transition from the kinetic overgrown (initial stage of the process) into the diffusion takes place in time. At the initial time  $t = 0$ , equation (3) yields:  $J = k C_0$ , i.e. the reaction proceeds in the kinetic region and its rate is determined by the speed of reaction. If we consider that the second form of the integral will probability decreases with increasing  $t$  faster, than  $e^{-t^2}$ , so the macroscopic reaction rate decreases with time.

In the limit for large  $t$ , we obtain:

$$J = C_0 \sqrt{\frac{D}{\pi t}} \quad (4)$$

### 3. RESULT AND ANALYSES

This process proceeds to the kinetic region of the diffusion. Table 1 shows data for calculating the rate constant of diffusion of arsenic in gallium depending on temperature.

Assuming that the crystal grows in the heavy of breakages steps atoms coming from the melt to the

interface with further propagation speed monomolecular layer to completely fill in the first place

**Table 1**– Dependence of the rate of diffusion of arsenic in gallium temperature

$1 / T \cdot 10^3 \text{ K}$	$k, \text{ cm}\cdot\text{c}$
0,93	0,0009
0,85	0,0021
0,79	0,0043

$$\rho_{kp} = \frac{a \cdot \varepsilon}{2kT \ln \alpha} \quad (5)$$

where  $a$  is the distance between atoms,  $\varepsilon$  – energy of one bond between atoms  $k$  – Boltzmann constant,  $\alpha$  – saturation associated with supersaturating equality  $\sigma = \alpha - 1$ .

As an example, to assess the relative importance of the rate of crystallization in the total rate of the process in terms of the method analyze present payment rate for this stage crystals of indium phosphide. Binding energy  $\varepsilon$  determined based on the heat of solution of phosphorus in molten indium:

$$\varepsilon = \frac{\Delta H}{2N} = 2,6 \cdot 10^{14} \text{ erg / at} \quad (6)$$

Table 2 shows the values of the critical radius of nuclei at different temperatures and supersaturating.

An estimate of the rate formation showed that at about a thousand degrees Celsius and 0.4 supersaturating, nucleation rate amounted to  $6,5 \cdot 10^6 \text{ s}^{-1}$ . Travel speed step at a thickness of the diffusion layer one hundredth centimeter can be determined from the relationship:

$$V = a^2 \cdot D \cdot \pi \cdot N_0 \cdot \sigma (\ln \frac{\delta}{a}) - 1 \quad (7)$$

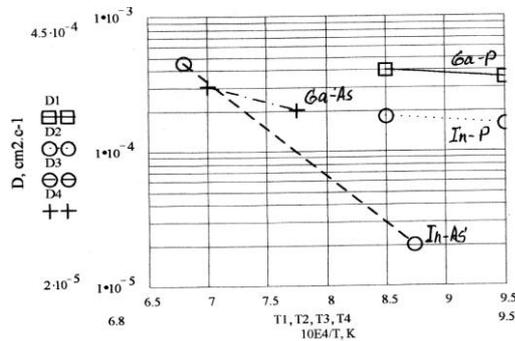
For the conditions above, the tangential speed of growth is 63.7 cm/s. Diffusive nature of the process is also confirmed by experiments to determine the dependence of the rate of crystal growth in terms of the temperature of this method.

The speed limit of the process rate of diffusion allowed using this method for the experimental determination of the diffusion coefficients of the fifth group in the melt element of the third group. Consideration of the kinetic features of diffusion in terms of the method reveals two kinetic region - region decreases (changing) the rate of diffusion and diffusion rate constant region.

**Table 2** – Dependence of the critical radius of the nucleus hypothermia at different temperatures

$T / \sigma$	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
1079	23,5	12,3	6,55	6,66	5,53	4,47	4,22	3,81	3,49
1093	23,1	12,0	8,39	6,54	5,43	4,68	4,05	3,75	3,43
1113	22,7	11,8	8,34	6,42	5,33	4,60	4,07	3,68	3,31
1133	21,9	11,4	7,95	6,20	5,15	4,44	3,94	3,55	3,25
1153	21,5	11,2	7,82	6,10	5,06	4,36	3,87	3,49	3,19
1173	21,5	11,0	7,69	5,99	4,97	4,29	3,80	3,43	3,14
1213	20,4	10,7	7,44	5,80	4,81	4,15	3,68	3,32	3,04

In the "stationary" stage of the process, when the rate of dissolution and crystallization were agreed, the temperature dependence of the diffusion coefficients was calculated. The results are shown on Fig. 3.



**Fig. 2** – Temperature dependence of the diffusion coefficients of phosphorus and arsenic in gallium and indium for the experimentally investigated temperature ranges

Crystallization synthesis method – solution-diffusion in the field of ultrasonic vibrations. The ultrasonic vibrations system comprising a resilient membrane which simultaneously serves as a lid of the container was developed. In the quartz reactor was charged gallium, or indium, arsenic, or phosphorus. The reactor was evacuated and sealed with a plug of quartz thickness of 0.1-0.2 mm. This plug is also served to excite ultrasonic vibrations in the reactor. The membrane is joined to a quartz rod derived from the furnace. With this rod ultrasonic vibrations transmitted to the reactor from an external source. In the process of growing melt treated frequency vibrations from 100 Hz to 100 MHz. The obtained ingot was cut perpendicular to the axis of cultivation plate thickness of 1 mm, whose surface was polished by a standard technique. The experimental results are shown in Table 3. From the presented data it is evident that treatment with ultrasonic vibrations causes the melt to improve the

homogeneity of ingots. The ingots with highest homogeneity were obtained at vibration frequency  $4 \pm 0,5$  MHz

**Table 3** – Coefficient of the optical transmission and frequency of the ultrasonic vibrations

No	Frequency of ultrasonic vibrations, MHz	The inhomogeneity of coefficient optical transmission %
1	–	9,0
2	0,001	7,8
3	0,005	7,7
4	0,01	7,0
5	0,1	7,9
6	1,0	7,4
7	1,1	7,3
8	2,0	7,5
9	3,0	6,8
10	4,0	6,2
11	5,0	6,7
12	6,0	7,1
13	10,0	7,0

#### 4. CONCLUSIONS

Comparison of the optimum frequency ultrasonic vibrations to increase uniformity in the mode of crystals convective transport under the Czochralski method and conditions of diffusive transfer indicates a significant difference between these frequencies, i.e. character determines the transfer conditions of optimization process. This fact must be taken into account when considering processes for the removal and in the vicinity of the solidification front.

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