Investigation of growing the $Hg_{1-x-y-z}A_xB_yC_zTe$ solid solutions by a modified zone melting method

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Abstract. This paper presents research of the process for growing the crystals of semiconductor solid solutions $Hg_{1-x-y-z}A_xB_yC_zTe$ under conditions of a modified zone melting.

Research of the process for zone melting of semiconductor solid solutions of $Hg_{1-x-y-z}A_xB_yC_zTe$ type is carried out in the works [1-3]. Contrary to [1], it is shown in [2, 3] that the size of variable-composition portions depends monotonically on the composition of the source polycrystal, and for $Hg_{1-x}Cd_xTe$ it is described by the empirical formula

$$C_s(z) = C_0\{1+b\cdot\exp(-(cz)^2)\}, \qquad (1)$$

where $b = 1.512\cdot10^{-2} + 0.22/x$, $c = 6.3\cdot10^{-2} + 0.31/x$ ($x = 0.16$ to 0.32), z is the distance from the ingot beginning, x determines a crystal composition, $C_s(z)$ and C_0 is the composition of ingot solid phase and the source polycrystal, respectively. In the paper [2], the Pfann equation is solved for zone melting, and it is shown that, for $Hg_{1-x}Cd_xTe$ ($x = 0.16$ to 0.32), the best agreement between calculated and experimental data is achieved by the linear approximation of the introduced distribution coefficient $R(z) = C_s(z)/C_0$.

In the work [3], a dependence of the distribution coefficient along the ingot length is derived, which is described either by the nonmonotonical function with a peak or by the monotonically increasing function achieving the saturation when reaching the homogeneous-composition portion.

This ambiguity of results and the appearance of new experimental data caused a more detailed research of the process for growing the mercury-containing semiconductor solid solutions of the $Hg_{1-x-y-z}A_xB_yC_zTe$ type under the modified zone melting.

Modification of the standard zone melting process lies in the following:

• an ampoule with a synthesized polycrystal is located at an angle to the horizon (the angle may vary within 30 to 45°).

• the ampoule is kept in permanent rotation around the longitudinal axis, thus agitating components in the melt zone.

The advantages of such modification are as follows. When growing the ingot at an angle to the horizon, the contact of liquid phase with polycrystalline ingot is practically achieved over the entire ingot length. It considerably reduces the influence of both gas interlayer and non-uniform dissolution of polycrystal. The agitation causes, firstly, the uniform dissolution of polycrystal; secondly, the reduction of temperature non-uniformity at a crystallization front, and, thirdly, reduction of the diffusion layer thickness at the crystallization front. It makes essential improvement both in axial and radial homogeneity of the resulting ingots. As shown in the experiments on drastic cooling of a melted zone, this approach provides the practically flat crystallization front, which is impossible to be achieved by other methods [4].

And, finally, in all probability, control of melted zone width will increase the yield of material of homogeneous composition, i.e., the composition that was planned when loading. A change in composition is to be observed only for $1 - 2$ lengths of melted zone at the beginning of ingot and at its end, when the liquid phase is no longer fed on polycrystal components. Needless to say, the length of variable-composition portions depends on the length of melted zone. Thus, varying the zone length, one can increase the yield of homogeneous-composition material, thereby reducing its cost.

For modeling a variable-composition portion we used two models. The first one [5] implies that segregation coefficient $K(z)$ (hereinafter we will use exceptionally this term without introducing the additional distribution coefficients) was considered to be dependent on a liquid phase composition as follows: $K(z) = a\cdot\exp(-bC_1(z))$, where a, b are the fitting
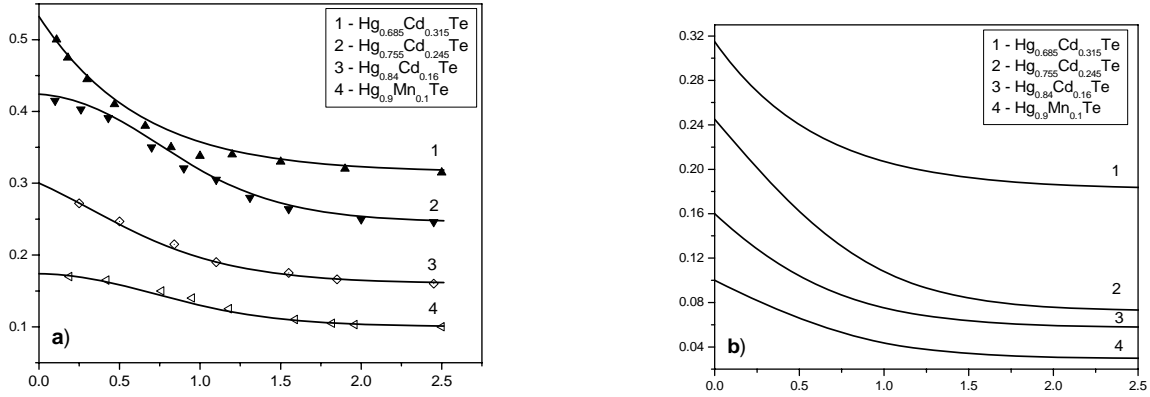
Fig. 1. Distributions of components along the ingot length in HgCdTe and HgMnTe crystals obtained by solving system (2) as compared with the experimental data in the solid phase of ingots (a) and in the molten zone (b).

parameters. The algorithm of solution was as follows. The system of equations was solved:

$$l \cdot dC_l(z) = (C_0 - K(z) \, C_l(z)) dz,$$
$$K(z) = a \cdot \exp(-bC_l(z)), \qquad (2)$$

where l is the molten zone length. There was the initial condition for differential equation $C_l(0) = C_0$. At the same time, the component concentration in solid phase was calculated as $C_s(z) = C_l(z)K(z)$.

The results of calculations are shown in Fig. 1 for HgCdTe of several compositions and HgMnTe.

As can be seen from the figure, the system of equations (2) provides an adequate description of experimental data obtained after the completion of the ingot growing (solid phase – Fig. 1a)). Really, at the distance of 1.5–2 zone lengths the curves flatten out, which corresponds to central ingot portion of constant composition. The behavior of curves calculated for the melt is similar, but their composition values are naturally lower.

Essentially, the second model is as followings. The segregation coefficient, like to that in the first model, was considered to be dependent on the liquid phase composition, however, this dependence was shown as a power series of the type: $K(C_l) = K_0 + K_1 C_1 + K_2 C_1^2 + K_3 C_1^3$. The functional dependence $K(z)$ was also restricted by the third-power polynomial: $K(z) = K_0' + K_1' z + K_2' z^2 + K_3' z^3$. The third polynomial power was chosen from considerations that this polynomial describes both the monotonically increasing functions and the functions with the peak found in the work [3]. The polynomial coefficients were chosen from the best fit of theoretical calculations to the experimental data. For this purpose, we used the successive approximation method, each step of it calculating the value

$$\Delta L = \sum_{i=1}^{n} \left| C_{si}^{exp} - C_s^{theor}(z_i) \right|, \qquad (3)$$

where n is the number of experimental points, z_i is the distance from the ingot beginning C_{si}^{exp} are experimental values of component concentration in the solid phase, $C_s^{theor}(z_i)$ are the calculated values of the component concentration at the same experimental points. Then the search for minimum ΔL value was started for each curve, upon achieving which the iteration process was stopped.

The results of calculations by this method are shown in Fig. 2.

Polynomial coefficients $K(C_l)$ and $K(z)$, as well as the values of ΔL, obtained as a result of calculations, are represented in Table. As can be seen from the figure and the table, this method offers a good precision. Theoretical curves show a good fit to the experimental data along the whole length of variable-composition portion. The segregation coefficient is described by monotonic curves, reaching the saturation when achieving the constant-composition portion. The value of the segregation coefficients for studied ingots varies

Table. Polynomial coefficients and the accuracy of segregation coefficient calculation.

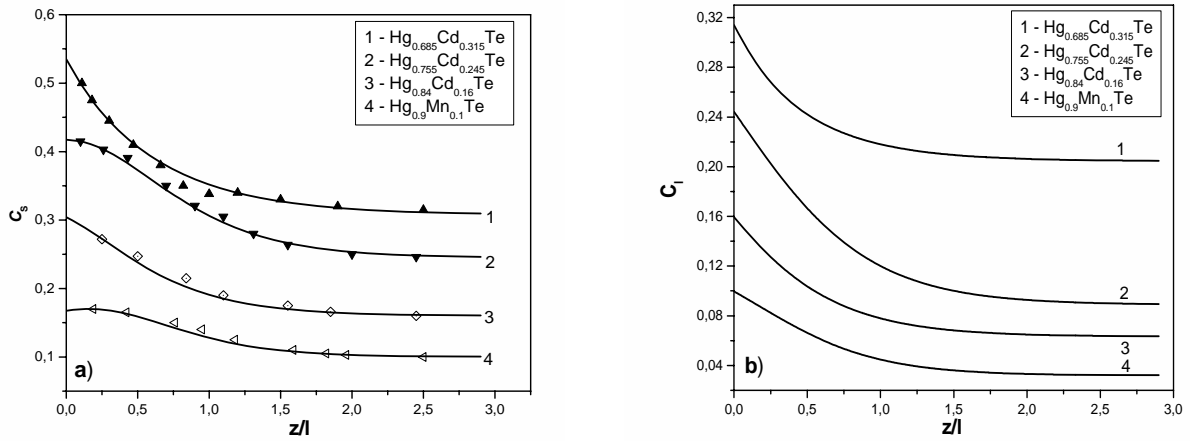| Segregation coefficient type	Curve number (Fig.2)	C_0	ΔL	K_0	K_1	K_2	K_3
$K(z)$	1	0.315	0.054	1.687	0.007	−0.015	0.001
	2	0.245	0.02	1.625	0.658	−0.118	0.007
	3	0.16	0.016	1.898	0.505	−0.065	0.003
	4	0.1	0.019	1.63	0.647	0.001	−0.004
$K(C_l)$	1	0.315	0.058	1.195	1.368	1.352	1.197
	2	0.245	0.034	3.336	−6.428	−1.109	0.61
	3	0.16	0.034	2.824	−3.951	−11.148	−1.421
	4	0.1	0.028	3.793	-20.761	−5.181	9.669

Fig. 2. Comparison of theoretical calculations to experimental data for three crystals of HgCdTe (curves 1-3) and one of HgMnTe (curve 4): composition distributions in the solid phase (a) and in the molten zone (b).

from 1.5 to 3.2. Thereof, it can be concluded that with the decreasing component concentration in the source polycrystal the segregation coefficient is increased. It reaches a peak in HgMnTe and varies from 1.7 to 3.2. The minimum segregation coefficient can be found in HgCdTe ($x = 0.315$), varying from 1.8 to 1.55 at the constant-composition portion.

As is evident from the foregoing research, the method proposed is in a good agreement with the experimental and literary data, allowing us to use it for other materials of the type under study.

This simple method can be used only to compare the component distribution in three-component solid solutions (HgCdTe, HgMnTe, HgZnTe, *etc.*). If the number of components increases, as it occurs in the multicomponent solid solutions, they cannot be compared directly on the basis of composition. In this

case, the only possible way for comparison is consideration from the viewpoint of the energy gap. Therefore, to compare the submitted results with a component distribution in a new five-component semiconductor solid solution $Hg_{1-x-y-z}Cd_xMn_yZn_zTe$, we had to convert all the submitted experimental data by using the energy gap approach.

For this case, the theoretical calculations were made by the same method (minimization of the expression (3)) modified to calculate the energy gap. The calculation results as compared with the experimental ones are depicted in Fig. 3. As can be also seen, in this case, the method proposed provides a good fit of theoretical results to the experimental ones.

As seen, the component distribution in the new solid solution $Hg_{1-x-y-z}A_xB_yC_zTe$ obeys the same regularities as in the rest narrow-gap semiconductor solid solutions
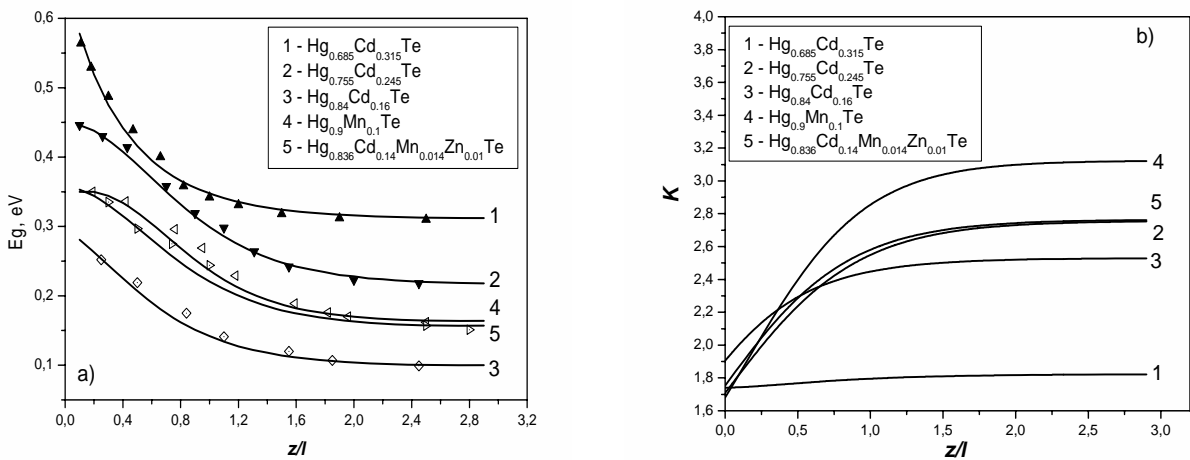

Fig. 3. Component distribution for multicomponent solid solutions of $Hg_{1-x-y-z}A_xB_yC_zTe$ type in the solid solution (a), as well as the segregation coefficient distribution (b).

of HgCdTe type. As regards to the energy gap at the homogeneous portion, this ingot is much the same as $Hg_{0.8}Cd_{0.2}Te$ and, obviously, $Hg_{0.9}Mn_{0.1}Te$. The segregation coefficient of $Hg_{1-x-y-z}A_xB_yC_zTe$ is also higher than unity and monotonously increases at the initial ingot portion with subsequent reaching the plateau. However, as can be seen from Fig. 3b, the segregation coefficient of $Hg_{1-x-y-z}A_xB_yC_zTe$ is practically identical to $Hg_{0.755}Cd_{0.245}Te$ one, varying from 1.175 to 2.75. In our opinion, this inconsistency is attributable to the presence of Mn and Zn in $Hg_{1-x-y-z}A_xB_yC_zTe$ crystal.

Based on the research performed, the following conclusions can be made:

- growth of multicomponent semiconductor solid solutions of $Hg_{1-x-y-z}A_xB_yC_zTe$ type is described by the segregation coefficient higher than unity;
- presentation of the segregation coefficient as the third-power polynomial $K(C_l) = K_0 + K_1C_1 + K_2C_1^2 + K_3C_1^3$ ($K(z) = K_0' + K_1'z + K_2'z^2 + K_3'z^3$) results in a good fit of theoretical results to the experimental data;
- the calculated segregation coefficients for solid solutions of $Hg_{1-x-y-z}A_xB_yC_zTe$ type monotonically increase from $1.7 - 1.9$ to $2.4 - 3.2$ at the initial ingot

portion and become saturated on reaching the constant-composition portion.

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