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## Isothermal growth kinetics of Cd<sub>x</sub>Hg<sub>1-x</sub>Te LPE layers

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**Abstract.** Within the diffusion-limited growth model, the kinetic analysis of the LPE process for Cd<sub>x</sub>Hg<sub>1-x</sub>Te solid solutions is carried out. It is assumed that a phase equilibrium exists on the interface, and the concentrations of components are connected by the equations of phase equilibria in the frame of the model of polyassociated solutions. These equations serve as the boundary conditions in solving the diffusion mass transfer problem. The developed thermodynamic model of growth allowed us to achieve the precision description of solid solutions, in particular to predict the regimes of the growth of layers with a given composition in the Cd-Hg-Te system.

**Keywords:** LPE, growth kinetics, semiconductor solid solutions.

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Nowadays Cd<sub>x</sub>Hg<sub>1-x</sub>Te solid solutions are widely used as components of infrared registration devices. Quite thick layers of the mentioned solid solutions are usually grown by LPE methods, by using various time-temperature regimes. The data on  $p$ - $T$ - $x$  phase equilibria in the system are supposed to be the main information while choosing the conditions of the crystallization process. For this system, the investigation of phase equilibria within the model of polyassociated solutions, which takes into account the presence of a set of complexes in the liquid phase, was started by us in [1, 2]. That's why, to increase the reliability of a thermodynamic information taken from the theoretical analysis, the kinetic assumptions about the phase formation process in the ternary system need to be developed.

The most complete kinetic description of the interaction between the liquid and solid phases during the formation of a heterostructure was carried out in work [3] with the use of the assumptions about diffusion mass transfer in the ternary systems of A<sup>3</sup>B<sup>5</sup> semiconductors. The offered software of solving the problem concerning the interaction kinetics of phases at LPE in the Cd-Hg-Te system was used in works [4, 5]. In those works, the modeling of the diffusion process in the interacting solid and liquid phases was carried out, and the influence of the mass transfer rate on the phase compositions and the interface motion was analyzed. Such data are necessary for revealing the general laws of processes running in the phases which are compositionally nonequilibrium. At the same time, the kinetic models of epitaxy with an appropriate choice of thermo-

dynamic functions and kinetic parameters allow one to describe the experimental data on LPE in solid solutions and to predict the technological conditions for the fabrication of materials with the given parameters with high reliability.

The assumption about the existence of a phase equilibrium on the interface underlies the diffusion-limited model. In works [4, 5], the equilibrium component concentrations on the moving interface were estimated, by using interpolation expressions for the description of phase equilibria in the Cd-Hg-Te system. Such dependences were obtained in [5, 6], by processing the experimental results on LPE in the system under consideration. It is known that the use of such an approach for the plotting of system's phase diagram without regard for the nonequilibrium of the crystallization can cause essential incorrectnesses in the calculated data and the loss of the thermodynamic information about system's behavior. The mentioned circumstances reduce the significance of the kinetic analysis of LPE carried out in works [5, 6] and require the further researches. Therefore, the purpose of the present work is as follows: to analyze the influence of the general parameters of the growth of layers on the composition and growth rate of solid solutions in the Cd-Hg-Te system on the basis of the diffusion-limited model, where the equations of phase equilibria for the polyassociative liquid phase are used as boundary conditions.

As known, the crystallization is limited by the diffusion of a substance to the “solid phase – melt”

interface. Thus, the thermodynamic equilibrium is supposed to exist on the surface boundary, which corresponds to the high rate of surface reactions. Then the problem of mass transfer to the interface includes the system of diffusion differential equations written down in the coordinate system moving together with the interface and the condition of substance conservation during its transition through the interface [3]:

$$\begin{aligned} \frac{\partial x_i}{\partial t} &= D_i \frac{\partial^2 x_i}{\partial z^2} + \frac{C_s}{C} V \frac{\partial x_i}{\partial z}; \\ \frac{C_s}{C} V (x_{s,i}^0 - x_i^0) &= D_i \frac{\partial x_i(0,t)}{\partial z}. \end{aligned} \quad (1)$$

Here,  $x_{s,i}^0, x_i^0$  are the solid and liquid phase equilibrium concentrations of the  $i$ -th component at the interface, respectively,  $D_i \frac{\partial x_i}{\partial z}$  – the components of fluxes reaching the interface;  $V(t)$  – the growth rate;  $\frac{C_s}{C}$  – the ratio of the molar densities of solid and liquid phases;  $i$  stands for particular solutes, Cd or Hg, and  $z$  – the coordinate axis directed into the melt.

In the presented expressions, the mass transfer into a growing solid phase is neglected. Such an assumption is justified by the small diffusion coefficients of the solid phase in comparison with their liquid phase analogs and the rather small times of growing system's existence under high-temperature conditions during the LPE process. The experience of calculations of the growth kinetics of  $A^3B^5$  solid solutions, by using parameters which are close to the real values of system's parameters, confirms the assumption stated above [7]. During the isothermal growth from the liquid phase supercooled by  $\Delta T$  at the initial interaction time, the melt can be considered as a semi-infinite liquid phase medium in relation to the concentrations of components at the interface [4]. Then the following expressions are the solutions of the diffusion equations under the conditions of matter conservation for each component during the phase transition [4, 7]:

$$\begin{aligned} x_{s,i}^0 - x_i^0 &= \frac{x_i^\infty - x_i^0}{\sqrt{\pi}(\lambda / \Delta_i^{1/2}) \cdot \exp(\lambda^2 / \Delta_i) \cdot \operatorname{erfc}(\lambda / \Delta_i^{1/2})}, \\ \lambda &= \frac{C_s}{C_i} \left( \frac{t}{D_{\text{Hg}}} \right)^{1/2} \cdot V(t), \\ h &= \int_0^t V(t) dt = 2 \cdot \lambda \frac{C_s}{C_i} \cdot (D_{\text{Hg}} \cdot t)^{1/2}; \quad \Delta_i = D_i / D_{\text{Hg}}. \end{aligned} \quad (2)$$

Here,  $x_i^\infty$  is the equilibrium concentrations of components of the initial melt;  $h, V(t)$  are the thickness and the growth rate of a layer, respectively; and  $D_i, \lambda = \text{const}$  are the diffusion coefficient of the  $i$ -th component and the growth rate parameter.

The above-given expressions, together with the equations of phase equilibria for the calculated concentrations of components on the interface,  $x_{s,i}^0, x_i^0$  [4], form the system of equations, which completely describes the isothermal growth kinetics of a ternary solid solution in terms of diffusion. The developed computing programs allows one to find the growing layer composition  $x_{s,i}^0$  and the melt component concentrations on the interface  $x_i^0$  versus the given initial melt composition  $x_i^\infty$  and the growth temperature or to calculate the composition of the initial liquid phase, which provides the crystallization of the given solid solution in the isothermal growth regime for the chosen  $T_g$  and  $\Delta T$ .

The analysis of the solutions of the diffusion mass transfer equation shows [7] that the terms of a semi-infinite liquid phase can be applied for the growth time intervals  $t < 0.2 \cdot L^2 / D$ , where  $L$  is the height of an initial melt, and  $D$  is the typical value of melt's component diffusion coefficient. According to the LPE process in the Cd-Hg-Te system, the growth time moment, up to which the assumption of a semi-infinite liquid phase is valid, for  $L \approx 1$  cm and  $D \approx 10^{-5}$  cm<sup>2</sup>/s, reaches several hours. This means that the mentioned approximation is quite applicable to typical conditions of the growth process.

The thermodynamic functions necessary for obtaining the boundary concentrations, which correspond to the conditions of phase equilibria in the Cd-Hg-Te system, were borrowed from our works [1, 2], where these parameters were found within the model of polyassociated solutions. The calculation of molar densities of the liquid phase enriched by tellurium and those of the Cd<sub>x</sub>Hg<sub>1-x</sub>Te solid solution was carried out using thermodynamic data [8]. According to our calculations, their ratio  $\frac{C_s}{C_i} = 0.955$ .

Naturally, the calculated composition and the growth rates of a solid solution depend on the chosen values of the partial diffusion coefficients of components. The above-mentioned discussion concerns to the diffusion coefficients of mercury and cadmium in a tellurium melt in a temperature range typical of LPE in the system. In the literature, such data are either extremely limited and inconsistent or found under conditions, being rather far from the LPE conditions. At the same time, precomputations have shown that the absolute values of diffusion coefficients significantly influence the growth rate and the thickness of a grown layer. Thus, the composition of a grown layer rather poorly depends only on the ratio of the diffusion coefficients of components. The last conclusion immediately follows from Eqs. (2), where the diffusion coefficients are connected with a parameter  $\Delta_i$  dependent on their ratio. Such a result allows us to choose the numerical values of diffusion coefficients not so strictly

and to consider them as the adjustable parameters of the model. The data in [9] are accepted as the first approximation while choosing the diffusion coefficients in the tellurium solution, where the temperature dependence of the mercury diffusion coefficient is described by the expression:  $D = 2.7 \cdot 10^{-3} \cdot \exp(-5200/R \cdot T)$  cm<sup>2</sup>/s.

It is possible to assume that the diffusion coefficient of cadmium should not considerably differ from the respective one of mercury, and it is quite reasonable to suppose that its temperature dependence is close to that offered in work [9].

As an initial information for testing the model, the experimental data [11-14] on the growth kinetics of solid solutions on (111)-oriented substrates were used. It is impossible to consider such experimental results completely correct. Really, it is known that the growth rate of (111)-oriented layers is 1.2-1.5 times less than the growth rate of (100)-oriented ones both for A<sup>3</sup>B<sup>5</sup> [7] and A<sup>2</sup>B<sup>6</sup> [15] semiconductors. At the same time, just for such an orientation of a grown layer, the most numerous and authentic experimental results are available [11-14]. Therefore, understanding the possible indeterminacies in the consequently found values of diffusion coefficients, it is possible nevertheless to consider such an approach as a reasonable one in the search for the crystallization model parameters.

The computations with the use of diffusion parameters from work [9] have shown the essential difference of experimental data on the thickness of epilayers and the less one of data on the grown solid solution composition. The insignificant updating of the values of diffusion coefficients has allowed achieving a quite satisfactory correspondence between the results of calculations and experiments on the composition and layer thickness versus the growth temperature and the layer thickness versus the growth time. The melt component diffusion coefficients found by the described method in the temperature interval 480-510 °C were independent of temperature:  $D_{Hg} = 2.6 \cdot 10^{-5}$  cm<sup>2</sup>/s and  $D_{Cd} = 2.9 \cdot 10^{-5}$  cm<sup>2</sup>/s. With their use, it was possible to quite satisfactorily describe the experimental data [11] on the solid solution composition dependence on the growth temperature and on the thickness of layers. These results are shown in Figs. 1-3. In Fig. 1, the grown layer composition versus the growth temperature for a fixed liquidus temperature of 501 °C is plotted. It is worth noting the quite satisfactory correspondence between the results of calculations and experiments on material's composition. Fig. 2 illustrates the calculated data on the epilayer thickness grown for 5 min versus the growth temperature with the same fixed liquidus temperature of an initial melt. It was noted earlier that the thickness of a grown layer essentially depends on the values of component diffusion coefficients. It is obvious from Fig. 2 that the data of work [9] on the mercury diffusion coefficient give an essential distinction between the calculated and experimental results both in a quantitative sense and in the slope of the temperature dependence of

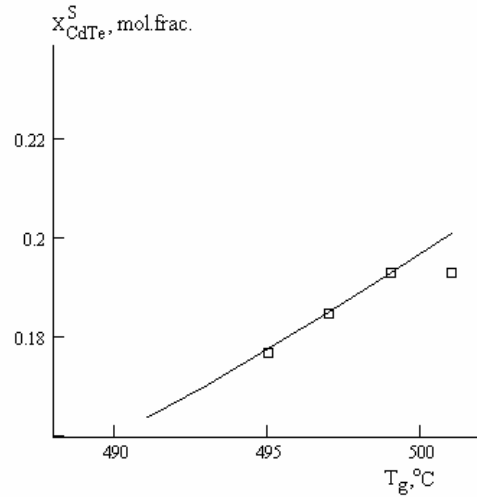


Fig. 1. Solid solution composition grown at various temperatures from the liquid phase with the concentration of initial components  $x_{Cd}^{\infty} = 0.006$  at. frac.,  $x_{Hg}^{\infty} = 0.216$  at. frac., which corresponds to a liquidus temperature of 501 °C; squares – data from [11].

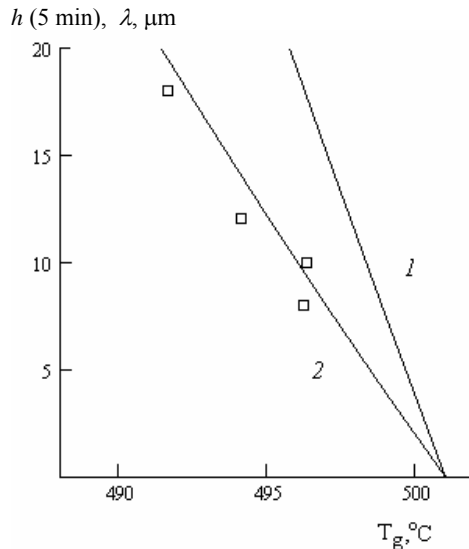


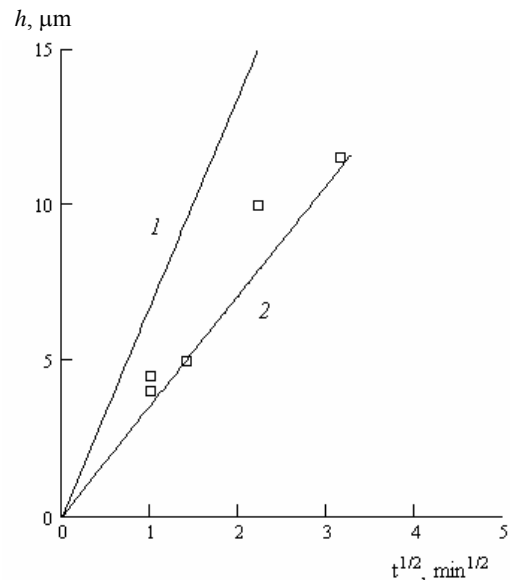
Fig. 2. Cd<sub>x</sub>Hg<sub>1-x</sub>Te solid solution layer thickness of  $x \approx 0.2$  mole frac., grown at different temperatures from the liquid phase with a liquidus temperature of 501 °C: squares – data of work [11], 1 – calculations with the use of data [9] on the mercury diffusion coefficient, 2 – our calculations.

the layer thickness. The latter can be related only to the enough weak temperature dependence of the diffusion coefficient, which was found in work [9]. In spite of the fact that the value of activation energy of the diffusion process in a melt according to data [9] correlates quite well with similar parameters for melts of other semiconductors, for example A<sup>3</sup>B<sup>5</sup> [7, 10]. Nevertheless, according to our results, it is necessary to consider its temperature dependence too weak in the given temperature range.

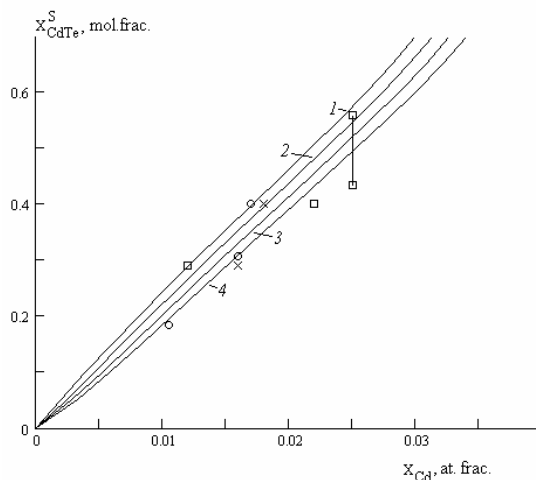
In Fig. 3, the plots of the grown layer thickness *versus* time for the initial liquid phase supercooled by 4 °C and the different values of diffusion coefficients are shown. The use of the coordinate axes ‘thickness – square root of growth time’ allows us to be convinced in the applicability of the variables related to a semi-infinite liquid phase for the description of the process, when the considered function is mapped by a straight line (2). A good correspondence of the calculated dependence to the experiment in the form and in a quantitative sense with the found values of diffusion coefficients confirms the applicability of the considered approximation to the description of the growth from a liquid phase of 1 cm in height for the given time interval.

In Fig. 4, the dependences of the cadmium content in a solid solution on its concentration in the initial liquid phase, which provides the growth of a material at the temperature  $T = 550\text{ }^\circ\text{C}$ , but with various initial supercoolings are shown. We also presented the experimental results of other authors [11-14] on the considered dependence obtained at somewhat different growth temperatures. Although the experimental results are very close to each other, the growth temperatures of layers differ rather essentially (about 20-30 °C). At the same time, at variations of the initial melt’s supercooling from 5 up to 15 °C, the calculated data completely superimpose the changing range of experimental results. This means that the kinetic effects concerning the melt’s supercooling have an effect for the grown layer composition variation approximately in a same way as the growth temperature change. We note that, as a rule, the liquidus temperatures in the mentioned experiments [11-14] were either obtained with a low accuracy or not controlled at all. Proceeding from the obtained results, the following conclusions can be made. Under essential distinctions in the solubilities of solid solution components, the kinetic correction for the initial melt supercooling can be very essential, and it should be taken into account while choosing an initial liquid phase composition. Especially, the account of the kinetic correction on a supercooling should be considered while plotting the phase diagrams of such solid solutions, by basing on the data on LPE in the system.

The observable correspondence of the results of calculations to the experimental data concerning the tendencies in the system’s behavior and in a quantitative sense confirms the applicability of the diffusion model to the description of the LPE process in  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  solid solutions. Thus, the approximation of the semi-infinite liquid phase for diffusion equations together with the polyassociative model of phase equilibria taken as boundary conditions can be efficiently used in the fabrication of layers with preset parameters under the given conditions.



**Fig. 3.**  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  solid solution layer thickness *versus* time of isothermal growth at various supercoolings of the initial liquid phase: squares – data [11], 1 – calculations with the use of data [9] on the mercury diffusion coefficient, 2 – our calculations.



**Fig. 4.** Solid solution composition *versus* cadmium concentration of the initial liquid phase at various supercoolings of the system. 1, 2, 3, 4 correspond to system's solidus line at  $T = 550\text{ }^\circ\text{C}$  and values of melt supercooling for  $\Delta T = 5, 10, 15\text{ }^\circ\text{C}$ ; squares – experimental data [12] for a growth temperature of  $550\text{ }^\circ\text{C}$ ; open circles, crosses – [13, 14] for  $500\text{ }^\circ\text{C}$ .

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