The composition modulation effect during spinodal decomposition of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ solid solutions under conditions of energy resonance

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Abstract. The Cahn-Hillard equation, previously obtained to describe the decomposition of metal solid solutions, is adapted to analyze the spinodal decomposition of $\text{A}_2\text{B}_6$ semiconductor solid solutions. The obtained differential equation is used to describe the spinodal decomposition of the $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ solid solution, which is synthesized under conditions close to the boundaries of absolutely unstable regions on the state diagram of the system. A quantitative description of the composition modulation effect that appears in the material when its growth under the indicated conditions is given.

Computer simulations of the spinodal decomposition of the $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ solid solution showed that micro oscillations of the material composition are connected by the resonance phenomenon between the excess mixing energy and the energy of elastic strains arising in the inclusions of the new phase coherently conjugated with the lattice of the initial crystal. It is shown that such resonance phenomena are most intense when the conditions for the material synthesis are chosen in the immediate vicinity of the spinodal curves in the phase state diagram of the system.

1. Introduction

$\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ solid solutions are a perspective material for electromagnetic radiation recorders for a wide range of wavelengths. Super thin layers of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ solid solutions are usually synthesized by vacuum technology at low temperatures on substrates (50-200\textdegree C) where growth is initiated \cite{1,2}. In this case \cite{3,4}, the temperature-concentration interval of the thermodynamic state of the $\text{Zn-Cd-Te}$ system is located near the region of spinodal decomposition of the material.

According to \cite{5,6}, the synthesis of solid solutions near the region of spinodal decomposition is accompanied by the formation of a peculiar periodic structure for composition of material. Periodic micro oscillations of the solid phase composition were found in a number of semiconductors solid solutions, primarily, class $\text{A}_3\text{B}_5$ \cite{10-12}. This effect is often called the effect of solid solution composition modulation. The formation of such composition structure in heterostructure: $\text{Ga}_x\text{In}_{1-x}\text{P}$ layer—a massive GaAs substrate, we analyzed thermodynamically and simulated numerically in \cite{7,8}. A successful description of the formation of a modulated structure in $\text{A}_3\text{B}_5$ solid solutions allows using a similar approach to simulate the spinodal decomposition of $\text{A}_2\text{B}_6$ solid solutions.
It should be noted that $A^2B^6$ solid solutions are often synthesized on an amorphous (non-oriented) substrate. In such situation, the deformation of the layer and the corresponding elastic component of the energy of the solid phase should be considered not with respect to the crystal lattice parameter (CLP) of the substrate [7, 8], but with respect to the CLP of the initial crystalline matrix of the material. The approach and results of solving this problem as applied to the description of the spinodal decomposition of Zn$_x$Cd$_{1-x}$Te solid solution under conditions of its low-temperature synthesis on non-oriented substrate are presented in this article.

2. Theory and mathematical tools for solving the spinodal decomposition problem

In [7, 8], the fundamental Cahn and Hillard equations [5–6] were adapted to describe the spinodal phase transformations during the decay of semiconductor solid solutions grown on a massive substrate. In this article, we consider the spinodal decomposition of solid solutions upon their preparation on an amorphous substrate or on substrates whose CLP is significantly different from the CLP of layers will be deposited. Such conditions correspond to the technological process in which polycrystalline layers of Zn$_x$Cd$_{1-x}$Te solid solution were synthesized on single-crystal silicon substrates or on glass [1, 2]. It should be noted that the silicon CLP differs from the CLP for all Zn$_x$Cd$_{1-x}$Te compositions by about ten percent. With such a significant discrepancy between the CLP layer and the substrate, there is no reason to expect coherent conjugation of these layers and, accordingly, conservation the elastic strains in system. In other words, in the absence of external factors that rigidly define the value of CLP in the system, the value of elastic deformations of new phases inclusions should be measured relative to the average CLP of the initial material crystal matrix. Therefore, when modeling the spinodal decomposition process for Zn$_x$Cd$_{1-x}$Te solid solutions in a wide compositions range, the CLP value of the solid phase matrix must be considered as a current variable associated with the average composition of the solid solution. This fact determines the fundamental difference between the approach of sloving the problem in the present work and the conditions for decay modeling, when the CLP of the deposited film is stabilized by the CLP of the substrate.

Under these conditions and with reference to Zn$_x$Cd$_{1-x}$Te semiconductor solid solutions, the stationary equation for calculating concentration fields has the form:

$$\frac{\beta d^2x}{dz^2} = \alpha_x x \cdot (1-x) + RT[x \ln x + (1-x) \ln(1-x)] + \lambda_{ijk} \cdot N_\sigma (a - a_\sigma)^2 / 4 - \mu,$$

where $z$ is the coordinate in the direction of the layer growth; $x$ is the molar fraction of zinc in Zn$_x$Cd$_{1-x}$Te; $N_0$ - Avogadro number; $\alpha_x, \alpha_\sigma, (\overline{x})$ - current and average CLP of the layer; $\lambda_{ijk}$ - combination of elastic moduli $C_{ij}$ [9]; $\beta$ - coefficient at the concentration gradient in the decomposition of free energy of the solid phase mixing [5, 6]; $\mu$ - chemical potential of the solid phase; $\alpha_x$ - parameter of interaction between the components of the solid phase according to the model of regular solutions; $R, T$ - gas constant and temperature.

The average concentration of the component in the solid solution was determined as:

$$\overline{x} = \frac{1}{L} \cdot \int_0^L x(z) dz,$$

where $L$ is the period of composition oscillation.

For the initial conditions, in which the composition range is set when modeling the material decay, as before in [7, 8], the expressions were used:

$$x_{init} = const, \frac{dx}{dz|_{z=0}} = 0.$$

The search for thermodynamic conditions under which periodic changes in the composition of the solid solution are realized was carried out by calculating the phase portraits according to the method [7, 8]. This approach allowed us to significantly accelerate the search for a set of initial conditions for the differential equation, which ensure the appearance of only oscillatory solutions. The numerical method for integrating the equation was based on the standard Runge-Kutta method.
3. Parameters of model

The distribution of components along the solid solution layer during its spinodal decomposition is determined by the excess energy of mixing of the components in the solid phase and elastic parameters of the solid solution matrix, i.e. elastic constants \(C_{ij}\). Elastic constants necessary for the simulation, as well as the CLP data for semiconductor compounds forming ternary Zn\(_x\)Cd\(_{1-x}\)Te solid solutions, are presented in [9]. Elastic properties of the solid solution, like its CLP, for each current composition were approximated by traditional linear equations written for each material parameter [7, 8].

It is fundamentally important to justify the choice of the solid-phase interaction parameter between main components of the Zn\(_x\)Cd\(_{1-x}\)Te solid solution. This parameter, which characterizes the excess free energy of mixing of components in the solid phase, is dominant not only in the description of the composition distribution in the equation being solved, but it sets the critical temperature of spinodal decomposition and the position of region boundaries of absolutely unstable and metastable states in the composition-temperature phase diagram. At the same time, the position of these boundaries is determined by intervals of thermodynamic parameters, where the application of the analysis is justified, and its results are most informative.

Despite limited experimental information on state diagrams of the Zn-Cd-Te system, especially at low temperatures, the available solid-state interaction parameters do not contradict their physical interpretation and their values correlate well with each other and with the data for other solid solutions of the A\(^2\)B\(^5\) system [3, 9]. Such situation justifies the possibility of using the results of [3, 9] in modeling the spinodal decomposition of considered solid solutions. The above considerations allow us to accept the following parameter value in our calculations:

\[ \alpha'_{Te-CdTe} = 17230 - 14.83 \cdot T \text{ J mol}^{-1}. \]

The critical decay temperature corresponding to the accepted interaction parameter was 547 K. In this case, we used the relationship between the interaction parameter and the critical temperature, known from the theory of simple solutions [3]:

\[ T_c = \alpha' / (2R). \]

The result of critical temperature calculations confirms the earlier conclusion that thermodynamic conditions for layer growth turn out to be very close to the boundaries of unstable states of the solid phase for Zn\(_x\)Cd\(_{1-x}\)Te solid solutions.

4. Modeling the modulation effect of composition in Zn\(_x\)Cd\(_{1-x}\)Te solid solution

The experimental data on modulation of the composition of A\(^2\)B\(^5\) solid solutions [10-12] were accepted as the initial data for modeling and estimating values of model parameters. As already noted, the fitting parameters of the model are the parameter of power series for the free energy corresponding to the solid solution \(\beta\) which is heterogeneous over its composition and constant \(\mu\). Moreover, the constant \(\beta\), in essence, sets only the period of oscillations in the solid solution composition. At the same time, the parameter \(\mu\), which is interpreted from the physical point of view as the chemical potential of the system during spinodal decomposition, sets the oscillatory process amplitude.

The parameter \(\beta\) value was estimated by us in [7-8] based on experimental data [10-12] on the compositional oscillation period (200–300 nm) in layers of Ga\(_x\)In\(_{1-x}\)P and Ga\(_x\)In\(_{1-x}\)P\(_y\)As\(_{1-y}\) solid solutions grown on GaAs and InP substrates. The parameter \(\beta\) is proportional to the square root of the oscillation period [7], and is a relatively weakly function of the input data. Based on this mathematical fact and the fact that for related systems of solid solutions the values of periods of composition fluctuations are close in magnitude, in the subsequent analysis, the parameter \(\beta\) was adopted the same as in [7-8], \(\beta = 0.06 \text{ J} \cdot \text{nm}^2 / \text{mol}\).

As for the amplitude of the oscillatory process, for almost all reported cases on the composition modulation effect in A\(^2\)B\(^5\) solid solutions, the oscillation amplitude did not exceed 0.02 mol.fr. [9-11]. This range of the oscillatory process is limited by the possibility of coherent conjugation of inclusions of the new phase and the crystal lattice of the initial solution, which is responsible for elastic stresses in the system. Indeed, higher oscillation amplitudes would inevitably ensure the excess of critical values necessary for the existence of an elastically deformed state of solid phase. The latter would lead to a breakdown of the oscillatory process. Therefore, in performed calculations, a \(\mu\) parameter value was found that would ensure the indicated oscillation amplitude.
As in [7–8], to find intervals of parameter \( \mu \) values, it used an approach based on the construction of a phase portrait for the analyzed equation. A fragment of the phase portrait, the curve for which is closed during the implementation of the oscillatory regime, is shown in Figure 1b. The presented closed loop in this portrait, which covers the stationary point of the differential equation \( \beta \frac{d^2x}{dz^2} = 0 \), and sets the interval of the parameter \( \mu \), which provides the necessary periodic solutions.

A typical periodic distribution of the composition over the layer of \( \text{Zn}_x\text{Cd}_{1-x}\text{Te} \) solid solution with \( \overline{x} = 0.19 \) mol%, which is synthesized at \( T = 400 \) K with constants found using the phase portrait of the equation, is shown in Figure 1a. As can be seen from the figure, concentration profiles of components differ significantly from the shape corresponding to harmonic oscillations. This is a consequence of the complex dependence of differential equation parameters for the distribution of concentrations on the material composition.

The calculation results in Figure 1a clearly illustrate the formation of concentration domains during the solid solution growth under thermodynamic conditions close to boundaries of spinodal decomposition. Note that the selected values \( \mu = -180 \) J / mol. and \( x_{\text{init}} = 0.21 \) mol.fr. for \( T = 400 \) K, there are located in close proximity to the stationary point at which resonance conditions between the energy causing the decomposition of the solid solution and the elastic energy created by inclusions of the new final phase are realized. The solution of equation is in close proximity to the resonance state, which is characterized by a significant increase in the amplitude of oscillations and, as a consequence, the manifestation of nonlinear properties of the initial equation.

Figure 1 also shows the experimental data on a typical value of the composition oscillations amplitude, which were observed when studying the composition modulation effect in \( \text{A}_3\text{B}_5 \) systems [10-12]. Calculations show that it is possible to ensure compliance with experiment only with special relationships between values of mixing energy, elastic energy, and the system chemical potential. Indeed, substantially large compositional variations in such process will cause the appearance of the large mismatch of lattice parameters in coherently conjugated materials.

![Figure 1](image_url)

**Figure 1.** Distribution of the composition along the \( \text{Zn}_x\text{Cd}_{1-x}\text{Te} \) solid solution layer synthesized at \( T = 400 \) K with an average composition \( \overline{x} = 0.19 \) mol.fr. (a) and the corresponding phase portrait for the initial differential equation (b). Experimental data is estimated on the base of data from [10-12].

Under such conditions, parameters of the system can exceed their critical values, which will lead to relaxation of the coherent state of the phases and disruption of the oscillatory process. In this case, the considered model is not applicable. The last argument allows us to make the following assumption. Since many factors must coincide in order to realize for the composition modulation effect in a solid solution, the effect under consideration should not be manifested in all cases when the growth system
is in a state close to the boundary of spinodal decomposition. Therefore, the composition modulation should be recognized as an effect that should rarely be encountered in the practical implementation of the process of obtaining ternary solid solutions.

**Figure 2.** The low-temperature fragment of the phase diagram of the Zn-Cd-Te system (a) and the dependence of the oscillations amplitude (b) arising at a material synthesis temperature of 400 K on the solid solution composition. 1, 2 — binodal and spinodal of the system; 3 is an 400 K isothermal section of the diagram, for which the simulation of the composition modulation effect was performed.

Figure 2 shows the results of modeling the effect of the spinodal decomposition of solid solutions at a growth temperature of 400 K for all material compositions. The calculated position of spinodals and binodals on the Zn-Cd-Te ternary system state diagram for the selected parameter $\alpha'$ was obtained using formulas from [3, 4]. Our calculations state that, as the composition of the solid solution approaches the boundaries of unstable and metastable regions, the fulfillment of the condition for the mixing energy coincidence and the energy of elastic deformations becomes more distinct. This is reflected in an increase in the amplitude of oscillations of the solid solution composition. In other words, the system implements conditions for the development of intense oscillatory processes, which are responsible for the appearance of the composition modulation effect in material. With a significant removal of the system thermodynamic state of from boundaries of material instability regions, resonance conditions are not satisfied. Therefore, it can be argued that the composition modulation effect in solid solutions is likely to be intense and can be experimentally detected when the system thermodynamic state is very close to boundaries of spinodal decomposition.

The appearance of periodic changes in composition should be taken into account during the formation of polycrystalline layers of solid solutions, when crystallite sizes become comparable with the modulation period.

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