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The Influence of New Phonon Branches on Spinodal Decomposition of Solid Solutions

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ABSTRACT: *In this paper, a theoretical study of the interface optical phonons role in the spinodal decomposition of semiconductor solid solutions is performed. The possibility of equilibrium decomposition is determined by the free energy temperature dependence. The contribution of the optical interface phonon potential to the free energy of the system is calculated. It is shown that it is the interface optical phonons that can determine the parameters of equilibrium modulated structures that are formed as a result of spinodal decomposition. The results obtained make it possible to determine the composition of individual layers and the period of the modulated structures.*
Keywords: *Modulated structures, Spinodal decomposition, Interface optical phonons, Nanostructures*

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I. INTRODUCTION

Homogeneous semiconductor solid solutions of $A_xB_{1-x}C$ type may decompose to yield composition-modulated structures with a macroscopic pseudo-periodicity (of the order of 100 – 1000 °A) in certain ranges of temperatures and compositions [1]. A number of such structures have been observed experimentally, for instance in [2-7].

The composition of the resulting layers has a fraction of atoms of type A equal to x_1 and x_2 which differ from the average composition of the solution x. Similarly, spontaneous formation of alternating layers of silicon carbide polytypes in the transition layer of the heterostructure occurs [8]. The variety of instabilities is responsible for the decomposition. As shown in [9], if the decay is almost equilibrium, thermodynamic instability is the main one. Such instability is determined by the competition of contributions to the free energy of chemical energy and mixing entropy. As the temperature decreases, the contribution of the mixing entropy becomes smaller and, at temperatures below a certain critical value of T_C, the solid solution becomes unstable. At temperatures close to the critical point T_C, the elastic interactions between the modulated structure layers are significant. As was shown in [10,11], such elastic interactions lead to the fact that the formation of periodic modulated structures becomes energetically favorable. Up to now, a number of fitting parameters have been required to describe the structures resulting from the decay. Difficulties were in the accurate determination of the chemical free energy.

II. THEORETICAL STUDY

In this paper, we propose a different approach for the theoretical study of the structures formed as a result of spinodal decomposition. It is based on taking into account the contribution to the free energy of excitations arising in the modulated structure, namely, interface optical phonons [12].

Let us consider a periodic structure with some characteristic period l arising as a result of spinodal decomposition of the semiconductor solid solution. The system under study consists of layers of the composition x_1 and the thickness a alternating with ones of the composition x_2 and the thickness b (see Figure 1).The main interest for us is the electromagnetic field of the interface optical phonons arising in the structure at the layer boundaries. For the correct determination of structure free energy, it is necessary to take into account the contributions of both the electric and the magnetic fields. If we neglect the small thickness of the interface region, then, as can be seen from Fig. 1, the structure period is defined as $l = a + b$.

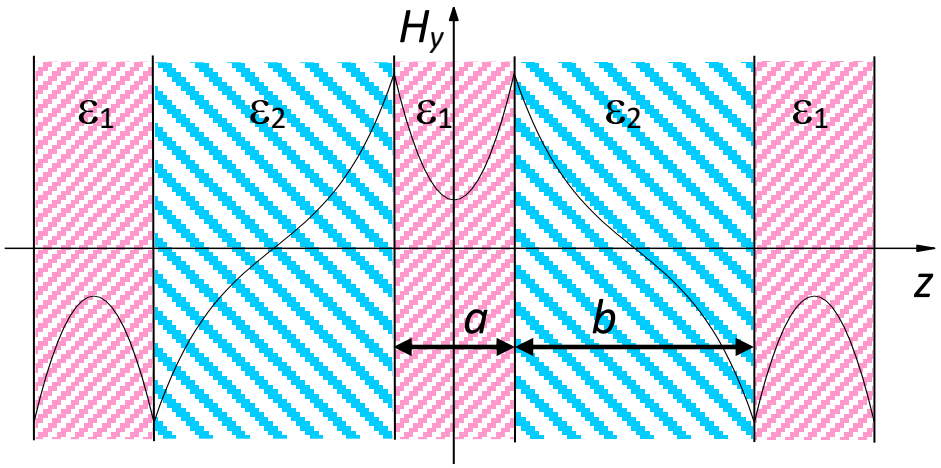

Figure 1: Distribution of the y-component of the magnetic field H_Y for interacting interface phonon modes.

As is known, the interface optical phonons arise at the interface between two media [13].One of these media has the negative dielectric function $\varepsilon_1(\omega) < 0$. The dielectric function of the another layer is positive $\varepsilon_2(\omega) > 0$. This condition is realized in the phonon frequency range at the interface between two layers of various compositions and corresponds to the dielectric function which is equal to

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\omega^2 - \omega_{LO}^2(x)}{\omega^2 - \omega_{TO}^2(x)}. \qquad (1)$$

Optical frequencies $\omega_{LO}^2(x)$ and $\omega_{TO}^2(x)$ depend on corresponding phase composition x_1 and x_2. This dependence leads to the appearance of a frequency interval in which the dielectric functions have opposite signs in neighboring layers. The interface phonons at different interfaces can interact with each other in a rather narrow region $ql \sim 1$ (here $q = (q_x, q_y, 0)$ is the two-dimensional wave vector). The z-axis in Fig. 1 corresponds to the structure modulation direction. It is convenient to choose the y - axis parallel to the magnetic field direction. As this take place, the magnetic field in the range $-a/2 < z < a/2$ has the form:

$$H_1 = H_0 e^{iqx} ch\chi_1 z, \qquad (2)$$

where H_0 is the magnetic field amplitude and the parameter $\chi_1 = \sqrt{q^2 + (\omega/c)^2 |\varepsilon_2(\omega)|}$.

In the region $a/2 < z < (a/2) + b$ the magnetic field can be written as

$$H_2 = \frac{ch\frac{\chi_1 a}{2}}{sh\frac{\chi_2 b}{2}} H_0 e^{iqx} sh\chi_2\left(\frac{l}{2} - z\right). \qquad (3)$$

Here $\chi_2 = \sqrt{q^2 - (\omega/c)^2 \varepsilon_1(\omega)}$. The magnetic field arising due to the interaction of the interface waves is symmetric with respect to the plane $z = 0$ and changes at equal intervals equal to *2l* in the subsequent layers. The magnetic field caused by the interface wave interaction is symmetric under $z = 0$ plane and varies at regular intervals equal to *2l* in subsequent layers. If the magnetic field is specified, we can obtain the electric field components from Maxwell's equations:

$$E_x = -\frac{ic}{\varepsilon\omega}\frac{\partial H}{\partial z}; \qquad E_z = \frac{ic}{\varepsilon\omega}\frac{\partial H}{\partial x}. \qquad (4)$$

To determine the interface wave spectrum, we substitute the continuity condition at the boundary of two layers for the electric field tangential component into equation (4) and obtain the following expression:

$$\frac{\chi_1}{\varepsilon_1(\omega)} th\frac{\chi_1 a}{2} th\frac{\chi_2 b}{2} = -\frac{\chi_2}{\varepsilon_2(\omega)}. \qquad (5)$$

The contribution of the interface optical phonon field to the free energy can be found as

$$\delta F_{ph} = \frac{2}{l}\left\{ \int_0^{a/2} \left[\varepsilon_1(\omega)\left(E_{1x}^2 + E_{1z}^2\right) + H_1^2 \right] dz + \right.$$

$$\left. + \int_{a/2}^{l/2} \left[\varepsilon_2(\omega)\left(E_{2x}^2 + E_{2z}^2\right) + H_2^2 \right] dz \right\} \qquad (6)$$

In the general case, the equation (6) for δF is the many-parameter problem. However, for small values of the vector q that satisfy the conditions $qa \ll 1$ и $qb \ll 1$, the expression (6) takes a simple form. This is the main assumption of our model. If we apply this assumption, then, in accordance with the equation (5) $|\varepsilon_2| \ll \varepsilon_1$, and the expression (6) takes the form:

$$\delta F_{ph} = H_0^2 \frac{a}{l}\left(1 - \frac{\varepsilon_1}{|\varepsilon_2|}\right) < 0 . \qquad (7)$$

The magnetic field amplitude H_0 can be expressed through the material parameters as follows. The amplitude of the optical vibrations of atoms i.e. interface optical phonons, with a frequency ω is equal to $u_0 = \sqrt{\hbar/\mu\omega}$. Here μ is reduced unit cell mass. The optical vibrations in ionic crystals give rise to an electric field with the amplitude $E_0 = \frac{\mu}{e}\left(\omega_{TO}^2 - \omega^2\right)\sqrt{\hbar/\mu\omega}$. The magnetic field amplitude H_0 in the long-wave approximation can be written as

$$H_0 = \sqrt{\frac{\varepsilon_2^2}{\varepsilon_1}} E_0 = \frac{|\varepsilon_2|}{\sqrt{\varepsilon_1}} \frac{\mu}{e}\left(\omega_{TO}^2 - \omega^2\right)\sqrt{\frac{\hbar}{\mu\omega}} . \qquad (8)$$

In accordance with the dispersion law (5), a negative sign of δF_{ph} means that an increase in the composition difference $x_1 - x_2$ leads to decreasing the volume free energy.Two phases with various compositions of solid solutions have different lattice constants.This difference, or mismatch, is a source of elastic stresses in the system. In accordance with Vegard's rule, when the difference $x_1 - x_2$ increases, the mismatch in the lattice constants also increases.

This leads to a larger elastic contribution δF_{el} to the free energy of the system. It has the form [10]:

$$\delta F_{el} = |x_2 - x_1|^2 \left(\frac{\Delta a}{a_0}\right)^2 \lambda , \qquad (9)$$

where $\Delta a = a_{AC} - a_{BC}$ determines the lattice constant mismatch for the extreme compositions of the solid solution $A_{1-x}B_xC$, a_0 is average lattice parameter of the solid solution, λ is the known combination of elastic modules. Energetically optimal compositions of different layers x_{opt1} and x_{opt2} can be found by minimizing the free energy

$$\delta F = \delta F_{ph} + \delta F_{el} \qquad (10)$$

It is necessary to take into account the particle number conservation during the decomposition process:

$$\frac{a}{l} x_1 + \frac{b}{l} x_2 = x_c . \qquad (11)$$

The value of x_c here is the average composition of solid solution before the decomposition.

Contributions δF_{ph} and δF_{el} to the equation (10) can be expressed in terms of parameters well known for various solid solutions.This gives us a good opportunity to determine the composition and period of the modulated structure resulting from the spinodal decomposition of such solid solutions. The difference in the compositions of the two phases corresponds to the minimum of free energy (10):

$$x_1 - x_2 = \frac{1}{2}\frac{a_0}{|\Delta a|}\sqrt{H_0^2 \frac{a}{l\lambda}\left(1 - \frac{\varepsilon_1}{|\varepsilon_2|}\right)} . \qquad (12)$$

III. CONCLUSIONS

Expression (12) connects the difference in the compositions of two phases with the macroscopic parameters of solid solutions in the phonon frequency region. For most semiconductor solid solutions, all the necessary parameters are known, although with varying degrees of accuracy. From the found values of the layer compositions x_1 and x_2, we can determine the period of the structure *l*. To verify and refine our model, it is

necessary to compare dependence (12) with experimental data for the concrete modulated structures resulting from the spinodal decomposition. Such a comparison would make it possible to establish whether the proposed mechanism is determining in the process of spinodal decay or, in addition to interface optical phonons, the contribution of other elementary excitations of the system should be taken into account. We plan to examine this in a future.A study using the parameters for a number of semiconductor solid solutions will be carried out by us as the next stage of work.

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