Periodic distribution of components in HgCdTe caused by laser treatment

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1. Introduction

Mercury cadmium telluride (MCT) – an most important material for infrared devices, has an essential fault: the weak HgTe bond. However, these peculiarities – the weak HgTe bond – have another aspect: the possibilities to modify the properties of that material by external influences, for example, by laser irradiation. In this paper it is shown that the diffusion processes of atoms at laser annealing of $Hg_{1-x}Cd_xTe$ can cause the specific conditions of decomposition of solid solution, which determine its inner periodic structure.

2. Changes of the free energy of a solid solution due to the local changes of the concentration

Having a two-component solid solution an equilibrium dependence of temperature T as a function of concentration C of one solution in another can be constructed from the temperature dependence of a free thermodynamical energy density f on concentration of the solution (Fig. 1). On the upper part of Fig. 1 it can be seen that the curve $f(c)$ has two minima at the temperature T_2 and T_3. Points O and O' represent inflexion points of the free energy curve. These points are very important because they separate a convex part of curve $f(c)$ from a concave one, whicht determines increasing or decreasing of the free energy of solution which undergos transition from a one-phase to two-phase (heterogeneous) solution. Minimum points of curve $f(c)$ for various teperature projected onto diagram $T(c)$ form an equilibrium diagram (Fig. 1b). Solid line on Fig. 1b is a line of the disolving and the domain under this curve represents a range in which two phases can exist together in the metastable state. The projection of inflexion points O, O' of all curves $f(c)$ on a diagram $T(c)$ forms a spinodal curve (dashed line in Fig. 1b) which separates the domain of points (T, c) for which the degradation of the solution can be spinodal only. The field between solid and dashed line in Fig. 1b represents the metastable superfused solid solution. In this range nucleons can be formed only by fluctuations of concentration, and this is the only way for degradation of homogeneous solution into heterogeneouso solution. Free energy for nonhomogeneous solution (with various concentration values in different points of solution) can be expressed as [6, 7]:

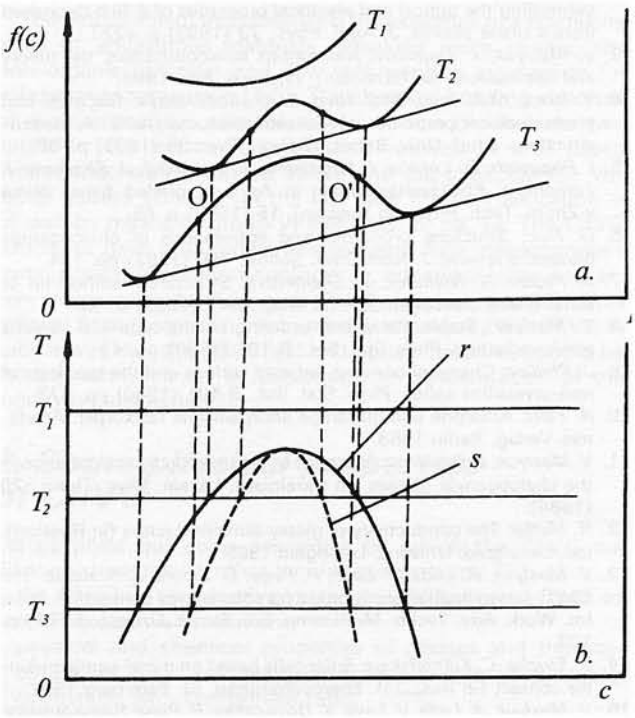

Fig. 1. The construction of the equilibrium diagram $T(c)$ of the two-component solid solution [5]

$$F = \int_v [f(c) + \frac{1}{2}\beta(c)(\nabla c)^2]\, dV \tag{1}$$

Formula (1) has been derivated for an isotropic solid solution and for solution in which the nonhomogeneity of concentration is continuous, i.e., the characteristic distance is greater than the atom potential interaction radius. In formula (1), $f(c)$ is free energy density, $\beta(c)$ is a function of composition, ∇ is Nabla operator and the integration is carried out over all volume of the crystal.

Lets calculate now a free energy change ΔF caused by a concentration nonhomogeneity.

$$\Delta F = F - F_0 \tag{2}$$

where F_0 is an energy of an onhomogeneous solid solution with average concentration $\bar{c}$

$$F_0 = \int_v f(\bar{c})\, dV = f(\bar{c})\, V \tag{3}$$

Using (1) and (3) one can express the energy change ΔF as

$$\Delta F(\{c(\vec{r})\}) = \int_v [\Delta f(c) + \frac{1}{2}\beta(\nabla c)^2]\, dV \tag{4}$$

where

$$\Delta f(c) = f(c) - f(\bar{c}) \tag{5}$$

From the equation (4) one can see that the energy change ΔF is a functional over function class $c(\vec{r})$.

3. Composition nonhomogeneites of solid solution in metastable state

A state of a homogeneous solid solution in a metastable phase corresponds to a minimum free energy on a hypersurface in a multi-dimensional space of concentration distribution functions. Each point of this space is determined by N coordinates beeing probabilities of occupation of N nodes by atoms of the same component. The system can be transformed from a metastable state to the state with an absolute energy minimum only by a lowest "pass" connecting both minima on that surface. Then the system takes a minimum energy change. Taking into account free energy changes determined by expresion (4), a variation of the functional ΔF in the saddle point should be equal to 0:

$$\delta \Delta F(\{c(\vec{r})\}) = 0 \tag{6}$$

Using conservation law of number of atoms of given componenets in a solution:

$$V\bar{c} = \int_v c(\vec{r})\, dV \tag{7}$$

the equation (7) can be expressed as:

$$\delta\Phi(\{c(r)\}) = 0 \tag{8}$$

where

$$\Phi = \int_v [\Delta f(c) + \frac{1}{2}\beta(\nabla c)^2 - \mu c]dV \tag{9}$$

is a functional of thermodynamical potential of the system, μ is a Lagrange multiplier playing role of the chemical potential. The expression (7) can be rewritten as

$$\delta\Phi = \int_v \left[\frac{d\Delta f(c)}{dc} - \beta\nabla^2 c\right]\delta c(\vec{r})dV = 0 \tag{10}$$

where $\delta c(\vec{r})$ is a variation of concentration distribution. Since variation is not equal to 0, the left side of equation (10) vanishes if

$$\frac{d\delta f}{dc} - \mu - \beta\nabla^2 c = 0 \tag{11}$$

Equation (11) is an Euler equation for variational problem. Solutions of this equation $c(\vec{r}) = c_0(\vec{r})$ indicate minimum, maximum and saddle points of the functional ΔF preserving the conservation law (7). Equation (11) is a differential equation of second degree in respect to the concentration distribution c. In [8] and [5] in chapter 5 it has been shown that onedimensional concentration distributions in solid solutions are more energeticaly convenient then multidimensional ones. Therefore in the onedimensional case equation (11) has the form

$$\beta\frac{d^2c}{dx^2} - \frac{df(c)}{dc} + \mu = 0 \tag{12}$$

The form of equation (12) resembles a form of a differential equation of harmonic oscillator

$$m\frac{d^2x}{dt^2} = -F(x) \tag{13}$$

where β, concentration c and the expression $(-\frac{df(c)}{dc} + \mu)$ in equation (12) plays the role of mass m, coordinate x and force F respectively in equation (13). Integral of motion for equation (12) is

$$E = -\left[\frac{p^2}{2\beta} - f(c) + \mu c\right] \tag{14}$$

where

$$p = \beta\frac{dc}{dx} \tag{15}$$

Comparing (14) and (15) we find differential equation of the first order

$$\beta\frac{dc}{dx} = \sqrt{2\beta(-E + f(c) - \mu c)} \tag{16}$$

Solutions of this equation are functions $c(x)$, i.e. concentration distribution functions. These solutions depend on two parameters: chemical potential μ and integral of motion E. Since chemical potential can be expressed by averaged concentration $\bar{c}$ and by integral E (using equation of number of atom conservation (7)), then solutions of equation (16) can be written in the form

$$c_0(x) = c_0(x, \bar{c}, E) \tag{17}$$

All solutions (17) can be divided into three parts which are responsible for three types of concentration distribution. They are represented graphically in Fig. 2. We can see that a decomposition of solid solution leads to the following macrostructure of solution:

a) two phases of solution with various concentration separated by intermediate range (Fig. 2a),
b) in any place of the solution the concentration is considerably increased; this case corresponds to the forming of one-dimensional nucleus (Fig. 2b),
c) periodic changes of concentration are created in the solution (Fig. 2c)

4. Metastable periodic concentration distributions

It is convenient to represent the state of solid solution in the configuration space, where for each concentration distribution $c(\vec{r})$ there corresponds a particular point in generalized phase space of distribution functions and corresponding to them free energy of the solution. Hence the decomposition process can be presented as a trajectory in phase space. This path starts in the configuration point which describes two-phase equilibrium state, and the point corresponds to absolute minimum of the free energy. All remaining points relate to transitional stages. The real shape of trajectory depends on the kinetics of the decomposition process. In the pecular cases the trajectory can pass by minimum points being not absolute minimum points. Concentration decompositions which relate to these points are metastable. Solutions of equation (16) coresponding to the metastable solid solutions appear in the case when thermodynamical potential has two minima on the different depth (Fig. 3a). Then for concentrations c_β^- i c_β^+ phase diagram takes the ellipse shape (Fig. 3b, curve β). Therefore such trajectory corresponds to a periodic distribution of concentration (Fig. 3c, solid curve). For concentrations c_α^-, c_α^+ we do not obtain the periodic distributions of concentration but a forming nucleus (Fig. 3c, dashed line). We can calculate the period a of

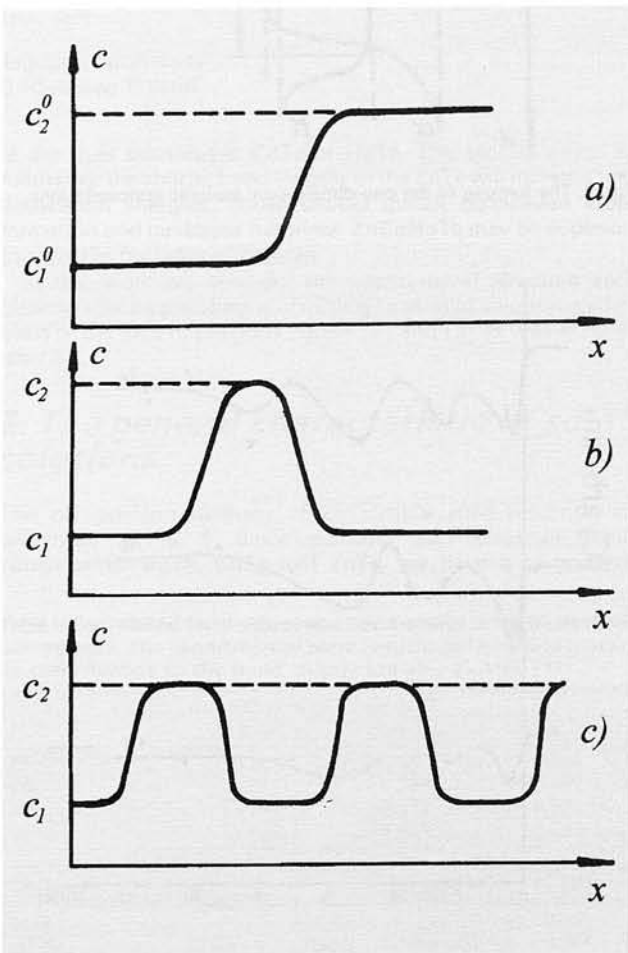

Fig. 2. Three types of the solution of equation (16)

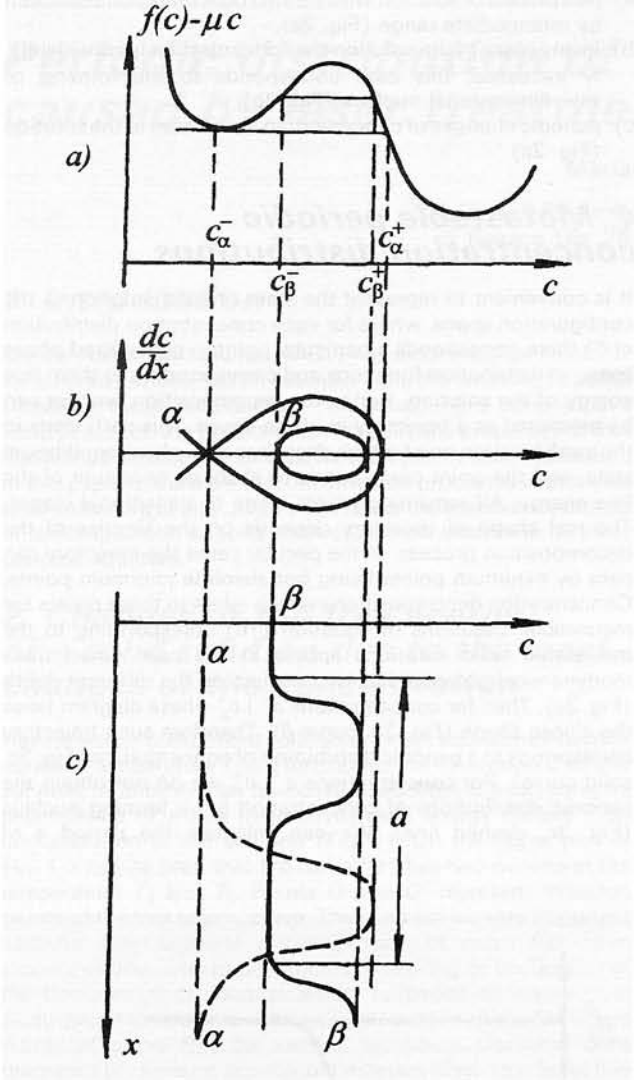

Fig. 3. The forming of the one-dimensional periodic concentrations

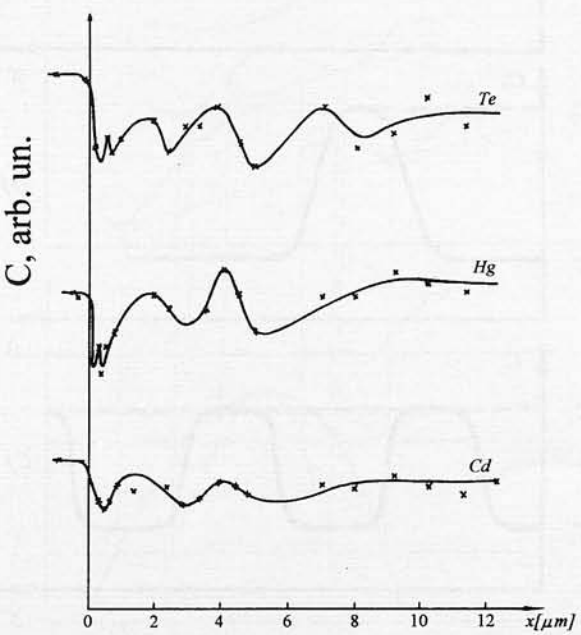

Fig. 4. Changes of the composition of $Cd_xHg_{1-x}Te$ after laser annealing

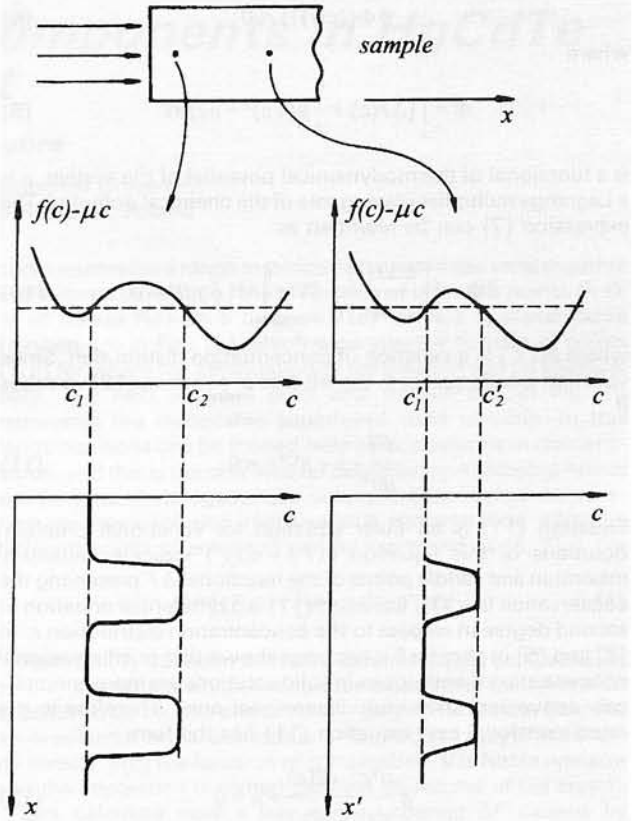

Fig. 5. Changes of the amplitude of concentrations oscillations in two points of the sample

concentration oscilations. For this purpouse we separate variables in equation (16), and by integrating both sides of the new equation we get

$$x - x_0 = \beta \int \frac{dc}{\sqrt{2\beta(-E + f(c) - \mu c)}} \tag{18}$$

where x_0 is an integrated constant and we can assume that $x_0=0$ for appropriatialy chosen origin of the coordinate system. With this we get following formulae for a period of concentration maxima

$$a = 0 \frac{\beta dc}{\sqrt{2\beta(-E + f(c) - \mu c)}} = 2\int_{c_\beta^-}^{c_\beta^+} \frac{\beta dc}{\sqrt{2\beta(-E + f(c) - \mu c)}} \tag{19}$$

5. Periodic coponent concentration distributions in CdHgTe

Crystals of the HgCdTe have been annealed without melting by pulsed YAG:Nd^{3+} laser. Parameters of the treatment were: energy density 0.8 J, time of the pulse 250 μs, number of the pulses: 1÷3. Electrical properties of such annealed crystals were described in several papers [9, 10, 11]. Results of measurements of component concentrations carried out by X-ray microanalysis point out on nonhomogeneity of distribution of components in the annealing layer [12, 13]. Changes of the chemical constitution of Cd, Hg, Te components are presented in Fig. 4. We can see that periodic maxima and minima of concentration appear in the layer, where laser radiation interacted thermally with a crystal. But these oscillations are not similar. The amplitudes of concentration decrease with the depth. These experimental results can be explained in the frame of the theory of the decomposition of

solid solution described in previous paragraphs. In the initial state, $Cd_xHg_{1-x}Te$ (x=0.2) forms a two-component homogeneous solution which consists of phase CdTe and HgTe with concentration c_1=20% and c_2=80%, respectively. Laser annealing causes heating of the material at a certain depth and then its rapid cooling. Due to the great temperature gradients the diffiusion of Hg atoms brings to the sharp maximum of Hg concentration at the 0,2 μm depth from the irradiated surface [13]. In this way two domains with different concentration appear in the material being by now homogeneous but with shaked thermodynamical equilibrium in the metastable state. Due to thermal fluctuations the solution undergoes transition to the state connected with a decomposition (metastable or even spinodal) forming a heterogeneous solution consisting of two phases CdTe and HgTe with mutable concentration. In this model, the amplitude changes of concentration oscilations with a depth x can be explained considering heating and cooling the material during laser annealing. A thermal history in various points of the sample is different. Therefore, the shape of the function $f(c)$ is different in each point x, what leads to the decreasing of the concentration amplitudes (Fig. 5).

6. Conclusions

HgCdTe solid solution is a specific material, in which diffusion processes are very sensitive to the external thermal conditions. This property appears particularily in the case of the laser annealing, where thermal conditions (temperature and temperature gradient distributions in time and space) are very extremal. The case investigated in this paper points out on the possibility of applying a such simple method like laser annealing to the construction of a periodic structures, which are similar to the quantum superlattices.

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