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MORPHOLOGICAL INSTABILITY OF SUBSTRATES OF $A^{III}B^V$ COMPOUNDS DURING HETEROEPITAXY FROM LIQUID PHASE

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The morphological instability of the phase boundary often appears during exposure of the multicomponent liquid phase of $A^{III}B^V$ compounds and the binary substrates. The deviation from the thermodynamic equilibrium of the heterosystem at the stage of the "liquid-solid" contact during heteroepitaxy of $A^{III}B^V$ compounds can lead in numerous instances to the so-called catastrophic erosion of the substrates. Catastrophic erosion of the solid phase surface manifests itself in selective etching (reaching considerable depth beneath the surface) or even in complete melting of the substrate during contact with liquid solution. The analysis of the energy balance at the exposure border of initially saturated liquid phase and the particular binary substrate enables to define the driving force of this effect. In the present paper, there are presented the results of analysis of the erosion processes in the Ga-In-P-As/InP system.

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1. Introduction

A disturbance of thermal equilibrium on the interface can lead, in numerous cases, to the so-called catastrophic erosion of substrates at the stage of exposure of liquid and solid phases during heteroepitaxy of $A^{III}B^V$ compounds. Catastrophic erosion of the surface of the solid phase manifests itself in its preferential etching reaching to a considerable depth or even in the entire melting of the substrate during contact with the initially saturated liquid solution [1]. Such effects are frequently observed when the multicomponent liquid solution reaches a saturation state before the exposure with the binary substrate. This effect is difficult to rationalise in terms of classically understood interphase equilibrium conditions, considering however the total energy balance of the heterosystem, it can be demonstrated that the interface, i.e. the region separating liquid and solid phases, has a significant effect on the intensity of various relaxation phenomena [2].

2. Theory

It should be stressed that every process of heteroepitaxial crystallisation of $A^{III}B^V$ compounds is based on the contact of the liquid solution with the binary substrate. The initial difference in the crystalline lattice parameters or in the radii of the mutually substituting atoms of the interface shifts the point of the thermodynamic balance of the system [1, 2].

The change of the total energy of the system connected with pseudomorphism, that is the coherent coupling of the region separating solid and liquid phases with the solid phase being the initial stage of contact of the liquid phase and the binary substrate, causes a shift of the point of thermodynamical equilibrium of the solution [2]. At the stage of pseudomorphism this shift is connected with the change in the saturation stage of the solution.

The described in the previous paper [2] analytical model of the interaction between the multicomponent liquid solution and the binary substrate of $A^{III}B^V$ compounds enables to determine condition of the quasi-equilibrium between the elastically deformed interface and the liquid phase for liquid phase heteroepitaxy of $A_xB_{1-x}C_yD_{1-y}$ type solutions, the equation describing relations between the chemical potential of compounds on the interface can be written as follows:

$$\begin{aligned} \Delta H_{ij}^F - T\Delta S_{ij}^F + RT \ln \frac{\alpha_i^l \alpha_j^l}{\alpha_i^{s,l} \alpha_j^{s,l}} = RT \ln xy + [y\alpha_1^s + (1-y)\alpha_2^s](1-x)^2 \\ + [x\alpha_3^s + (1-x)\alpha_4^s](1-y)^2 - [\alpha_c^s + x(\alpha_2^s - \alpha_1^s) + y(\alpha_4^s - \alpha_3^s)](1-x)(1-y) \\ + N_0 \left\{ \left[\left(\frac{Kq^2}{4\pi\epsilon_0 a_s} - \frac{A}{a_s^m} \right) - \left(\frac{Kq^2}{4\pi\epsilon_0 a_0} - \frac{A}{a_0^m} \right) \right] + n \frac{da_0}{dn_{ij}} \left(\frac{A(m-1)}{a_0^{m+1}} - \frac{A(m-1)}{a_s^m a_0} \right) \right\} \\ + \frac{N_0}{2} \left[\sum_{i,j=1,i \neq j}^4 n_{ij} (k_i \Delta R_i^2 + k_j \Delta R_j^2) + nn_{ij} (k_i \Delta R_i^2 + k_j \Delta R_j^2) \right]. \quad (1) \end{aligned}$$

In these equations, $ij = AC, AD, BC, BD$, $\alpha_{i(j)}^l$ and $\alpha_{i(j)}^{s,l}$ are the parameters of mutual interactions of component $i(j)$ in the liquid (l) and in the stoichiometric solution (s,l), ΔH_{ij}^F is the enthalpy of melting, ΔS_{ij}^F is the entropy of melting, ΔR_i is the difference in the atomic radii of corresponding elements of the interface and substrate, k_i is the elastic constant of A, B, C or D element, n is number of moles, q is the ionic charge, N_0 is the Avogadro number, ϵ_0 is the dielectric constant, A and m are the constants [2], $a_0 = f(x, y) = xy a_{13}(1-x)ya_{23} + x(1-y)a_{14} + (1-x) \times (1-y)a_{24}$ is the lattice constant of $A_xB_{1-x}C_yD_{1-y}$ -type solutions, a_s is the lattice constant of the substrate, respectively, $\alpha_c^s = \alpha_{13}^s - \alpha_{24}^s - \alpha_{23}^s - \alpha_{14}^s$; $\alpha_c^l = f(T)$ [3], $\alpha_1^s = \alpha_{AC-BC}^s$, $\alpha_2^s = \alpha_{AD-BD}^s$, $\alpha_3^s = \alpha_{AC-AD}^s$, $\alpha_4^s = \alpha_{BC-BD}^s$, $\alpha_i^l = f(T)$.

Solution of Eqs. (1) describing the quasi-equilibrium diagram on the interface [2] for the initial composition of the liquid phase (denoted by x and y molar indices of the equivalent solid solution) enables to determine the interface temperature and the composition of the liquid phase. The analysis of the obtained results enables to evaluate the effect of particular substrate on the saturation degree of the solution on the interface.

3. Results

Solution of the system of equations describing the interphase equilibrium coherent diagram [2], for the given, initial composition of the liquid phase enables to determine the interface temperature T^{int} of such a heterosystem for the isothermal exposure stage of the Ga-In-P-As solution with the InP substrate. The three-dimensional diagrams of such relations are depicted in Fig. 1. The thermodynamic parameters used in calculations were taken from Ref. [4].

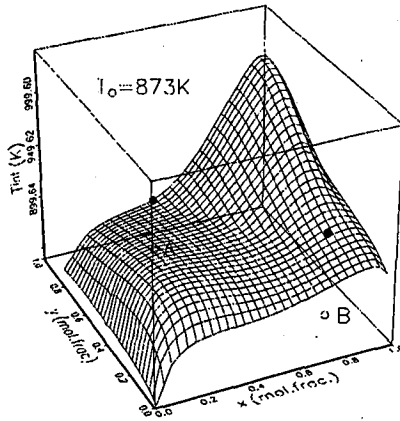


Fig. 1. Temperature of interface at the stage of exposure of $\text{Ga}_x\text{In}_{1-x}\text{P}_y\text{As}_{1-y}/\text{InP}$ heterosystem.

Analysis of temperatures at the interface of the considered heterosystem and the starting solution (Fig. 1) leads to the conclusion which of initial compositions shifts the point of thermodynamic equilibrium to a degree significant for the stimulation and growth of instability at the surface separating phases. In fact, the published in the literature information on the anomalous behaviour of some substrates at the contact with the saturated liquid solution [1, 5-7], as well as effects observed in the present paper, support the thesis of necessity of compensating the excess energy of the interface through the oversaturation of the solution. As the heteroepitaxy is mostly carried out in the closed system, the oversaturation of the liquid phase, during the isothermal exposure, has to be performed at the exposure of substrate etching.

In the case of significant shift from the point of thermodynamic equilibrium, which may be observed in the $\text{Ga}_x\text{In}_{1-x}\text{P}_y\text{As}_{1-y}/\text{InP}$ system, the fluctuational disturbance of the solution homogeneity can take place at the interface and etching of solid phases can proceed in a selective way. Figure 2 shows the thicknesses of the eroded layers as a function of the initial mismatch.

The contribution of the interface energy to the erosion process of substrates is additionally supported by the dependence of the dissolution depth on the initial mismatch of the liquid solution and the binary substrate (Fig. 2). Because of that, depending on the exposure conditions of the solution and the substrate, the subsurface layer can be either eroded to a shallow depth or even dissolved.

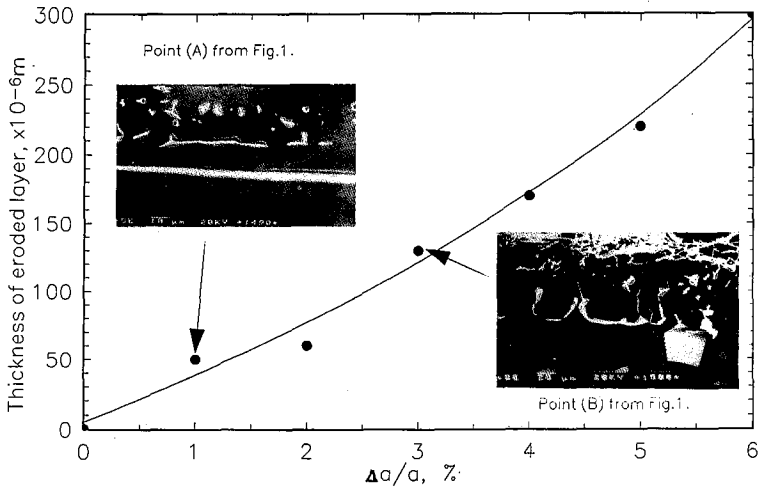


Fig. 2. Dependence of the dissolution depth on the initial mismatch, exposure time of 10 min.

4. Conclusion

The effect of catastrophic erosion appears during heteroepitaxy from liquid phase and is absent in homoepitaxial processes. Therefore, it can be stated univocally that this effect occurs for systems, in which interface surface is deformed due either to the initial difference in crystalline lattice parameters of contacting phases or due to the difference in the radii of mutually substituted atoms of solution and substrate. It follows from the performed observations and simulations that the driving force of such relaxation phenomena is the configuration energy of the interface region.

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