# FORMATION OF MULTICOMPONENT LAYERS IN THE SYSTEM $In - Ga - As - P$ IN LIQUID PHASE EPITAXY

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***Abstract.*** *The fabrication of semiconductor quantum electronic devices based on InP/GaInAsP heterostructures requires the growth of defect-free epitaxial layers. The growth of such epitaxial layers requires in-depth study and analysis of technological processes. This work demonstrates the possibility of growing epitaxial layers* $In_xGa_{1-x}As_yP_{1-y}$ *with a density of threading dislocations not exceeding* $10^5$ *u* $10^6$ $sm^{-2}$*, from a thin gap in liquid phase epitaxy. Using the example of a heterosystem* $In_{0,17}Ga_{0,83}As/GaAs$ *Various options for the formation of complex buffer layers necessary for the production of quantum electronics devices have been studied.*

***Keywords:*** *buffer layer, graded-gap, heterogeneous, heterojunction, heterostructure, heteroepitaxial growth, composition gradient, liquid phase, liquid-phase epitaxy, quantum electronics, lattice parameter, solubility, composition of the liquid phase, structural perfection, solid solution, solid phase.*

The process of liquid-phase epitaxial growth is a heterogeneous process occurring at the liquid-liquid interface solid. Analysis of the conditions of contact of the substrate with a nonequilibrium liquid or gaseous phase [1–4] indicates the complexity of the contact phenomena occurring at the interface. In this regard, the preparation of substrates for epitaxial growth can be of decisive importance for the growth of structures [5, 6] necessary for the manufacture of quantum electronics devices. InGaAsP solid solutions are widely used to produce quantum electronics devices, laser diodes, superluminescent radiation sources, and photodetectors [7–14]. The uniqueness of these structures lies in the fact that InGaAsP solid solutions are isoperiodic to gallium arsenide and indium phosphide, which makes it possible to create “ideal” heterojunctions suitable for wide application in instrument making [15–18].

There are a number of known methods for obtaining such heterostructures: the liquid phase epitaxy (LPE) method [4, 19], the molecular beam epitaxy (MBE) method [20, 21], and the metalorganic compound growth method (MOCVD) [22–24]. All these methods are aimed at creating heterostructures, which are the basis for quantum electronics device chips. The creation of chips from structures grown by MBE and MOCVD methods requires imported equipment and a unique post-growth technology for processing the structure, which complicates and increases the cost of the technological cycle of device manufacturing, requires high-precision and expensive technological equipment, and, moreover, occurs under conditions of non-equilibrium growth, which complicates their creation on profiled surfaces.

At the same time, methods are known for producing epitaxial heterostructures on profiled surfaces [25, 26], allowing simplify the technological cycle and create quantum electronics device chips using a relatively simple and cheap LPE method using domestic equipment from melt solutions in growth regimes close to equilibrium. Under such growth regimes, it is possible to create device structures with a high degree of layer perfection by simply doping different layers of

the structure over a wide range range of dopant concentration. By forming the initial profiled surface of the substrates, it is possible to carry out a selective growth regime on various faces, thereby creating a specified electrical and optical limitation for the passage of light in laser diodes. When growing epitaxial layers from the liquid phase, the orientation and mismatch of the lattice parameters of the substrates play an important role.

The purpose of this work is to demonstrate using the example of a heterosystem $In_{0,17}Ga_{0,83}As/GaAs$ various options for the formation of complex buffer layers, in which the (average) value of the composition gradient in the growth direction is effectively reduced.

In relation to the system $In_{0,15}Ga_{0,85}As/GaAs$ the authors of [27] showed that films with a dislocation density less than $10^6\ sm^{-2}$ can be obtained only if the composition gradient of the buffer layer $InGaAsP_{var}$ is no more than 0,2 at.% *Р/мкм*. Our studies of the same heterosystem have shown the successful growth of single-layer heterocomposites $In_{0,05}Ga_{0,95}As/InGaAsP_{var}/GaAs$ и $In_{0,1}Ga_{0,9}As/InGaAsP_{var}/GaAs$ with a density of threading dislocations not exceeding $10^5$ and $10^6\ sm^{-2}$, respectively (thin gap growth method, solution layer thickness 0.5 mm). However, for heterostructures $In_{0,17}Ga_{0,83}As/InGaAsP_{var}/GaAs$ This growth technique turned out to be unsuitable: films $In_{0,17}Ga_{0,83}As$ had the size $N_D$ more, than $10^7\ sm^{-2}$, even if at the heteroborder $GaAs/InGaAsP$ the relative discrepancy between lattice parameters was less $10^{-3}$. The composition gradient of the buffer layer was about 2 at.% *Р/мкм*, and the structural perfection of the heterocomposition deteriorated locally in different areas of the growing buffer layer due to the formation of thick growth steps. Thus, the task boiled down to finding a way to reduce the composition gradient in the direction of growth.

It would seem that in such a system, where a smooth transition in composition is ensured by the rapid depletion of the solution with a strongly segregating component (phosphorus), the desired reduction in the composition gradient can be achieved using two traditional ways: 1 – increasing the thickness of the solution layer on the substrate; 2 – increase in initial growth temperature $T_0$. In the first case, an increase in the thickness *l* of the solution layer on the substrate requires a decrease in the cooling rate of the system in proportion to $l^2$ therefore, obtaining one layer becomes a lengthy process. In the second case, an increase in temperature $T_0$ leads to increased solubility $GaAs$ in liquid phase $In-Ga-As-P$, which contributes to an increase in the thickness of the buffer layer $InGaAsP_{var}$. However, with increasing temperature, the phosphorus distribution coefficient decreases. Therefore, in order to match the initial part of the layer $InGaAsP$ with backing $GaAs$ according to the lattice parameter, necessary when increasing $T_0$ increase the amount of phosphorus in the liquid phase. This, in turn, reduces solubility $GaAs$. Therefore, the gain in film thickness is not as significant as one might expect, and the expansion of the temperature range leads to an increase in the deflection of the structure due to different temperature expansion coefficients (TEC) of the film and substrate.

The solution to the problem, in our opinion, was to obtain films $In_xGa_{1-x}As$ ($x \geq 0{,}15$) using multilayer compositions like $InGaAs/InGaAsP_{var}$. In fig. 1 schematically shows the change in the lattice parameter along the thickness of various compositions of variable composition, having a composition on the final surface $In_{0,17}Ga_{0,83}As$. Here curve 1 represents a single-layer heterocomposition $In_{0,17}Ga_{0,83}As/InGaAsP_{var}/GaAs$, and curves 2 and 3 are, respectively, two- and three-layer structures, where each layer is matched by lattice parameter or with the substrate $GaAs$, or with an intermediate composition using a transition layer in composition $InGaAsP_{var}$.

From Fig. It can be seen from Fig. 1 that in two- or three-layer structures there is an effective decrease in the composition gradient in the direction of growth.

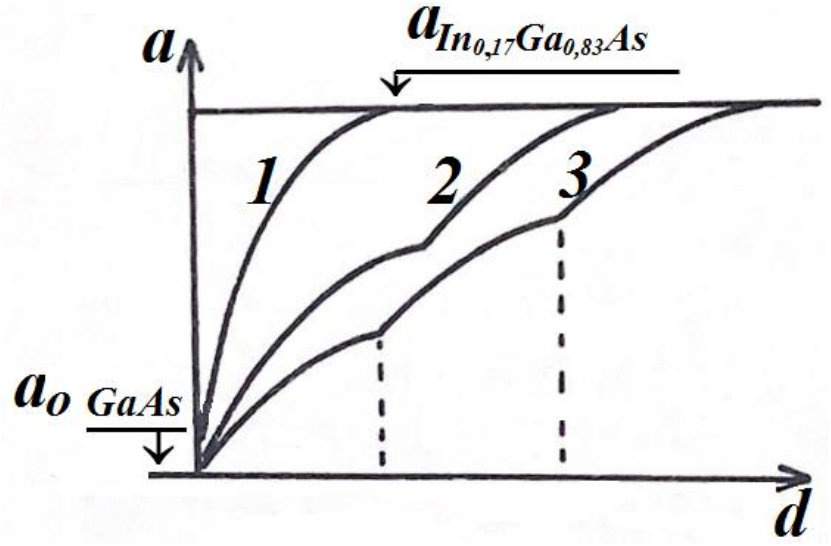


***Fig.1.***

Transition to this film growth technique $In_{0,17}Ga_{0,83}As$, at first glance, should be quite difficult, since at the stages of obtaining the second and subsequent layers a new selection of the composition of the liquid phase is required. It turns out that the compositions of melt solutions $In-Ga-As-P$ to create a multi-layer composition like $In_{0,17}Ga_{0,83}As/InGaAsP_{var}/In_{0,1}Ga_{0,9}As/InGaAsP_{var}/In_{0,05}Ga_{0,95}As/InGaAsP_{var}/GaAs$ can be calculated using solubility data $GaAs$ in liquid phase $In-Ga-P$ and experimental dependences of lattice parameter mismatch $GaAs$ and initial film $InGaAsP$ functions of the composition of the liquid phase (i.e. $\Delta a/a = f(X_P^L)$ ) for three basic liquid phase compositions $In-Ga-As-P$, from which single-layer compositions are obtained $In_xGa_{1-x}As/InGaAsP_{var}/GaAs$ с $x = 0{,}05; 0{,}1$ и $0{,}17$. These dependences must necessarily be and were obtained by us at the stage of radiation growth of single-layer structures with buffer layers $InGaAsP$ variable composition. Below we will show an example of such a calculation of liquid phase compositions $In-Ga-As-P$.

Figure 2 shows fragments of arsenic solubility ($GaAs$) in liquid phase $In-Ga-As-P$ ($In-Ga-P$), and in Fig. 3 – schematically the dependence of the mismatch of the substrate lattice parameters $GaAs$ and initial film $InGaAsP$ ($\frac{\Delta a}{a} = f(X_P^L)$ ) for three basic liquid phase compositions. The composition of the solution to obtain the 1st layer of a multilayer composition, for example, $In_{0,05}Ga_{0,95}As/InGaAsP_{var}/GaAs$ (III)A determined as usual: in Fig. 2 this composition is indicated by an arrow $\boldsymbol{a}$ and corresponds to the equilibrium solid phase $InGaAsP$, agreed with $GaAs$ (point *a* in Fig. 3). After growing the film in a temperature range sufficient for the disappearance of phosphorus in the solid phase (for example, $\Delta T \sim 50 \div 70$ K) we have a new complex substrate on the surface of which there is a solid solution of the composition $In_{0,05}Ga_{0,95}As$. In Fig. 3, its lattice parameter exceeds $GaAs$ marked with an arrow $\boldsymbol{b}$. Film growth can begin on this surface $In_{0,1}Ga_{0,9}As/InGaAsP_{var}$, initial excess of the lattice parameter over $GaAs$ which has the same (arrow $\boldsymbol{b}'$ ). Accordingly, the composition of this new liquid phase can be selected at 770 $^0$C: arrow $\boldsymbol{b}''$ on Fig.3 and arrow $\boldsymbol{b}$ on Fig.2.

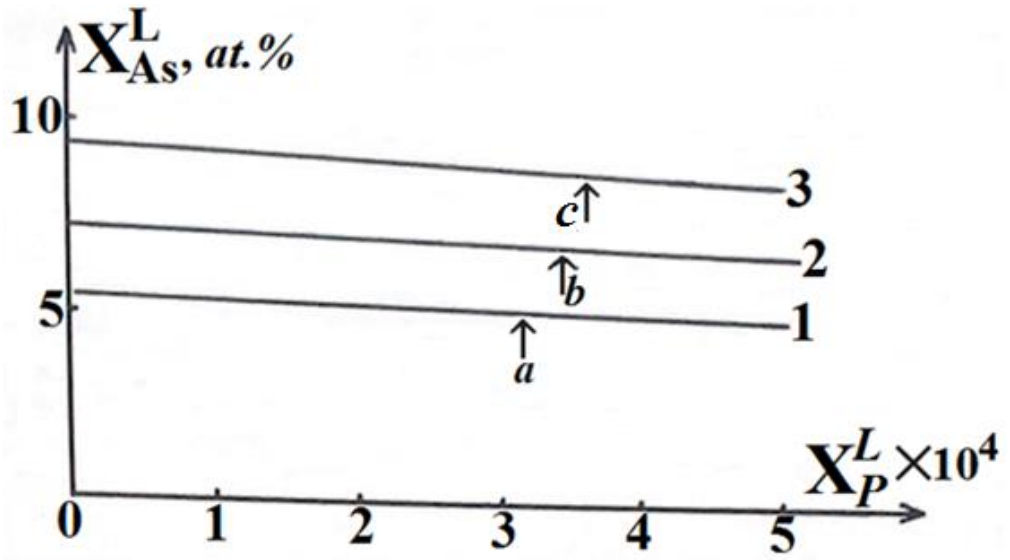


*Fig.2. Fragments of the solubility diagram of arsenic in the liquid phase $In-Ga-As-P$: curve 1 – basic composition of the liquid phase for obtaining films $In_{0,05}Ga_{0,95}As$; curve 2 – same for films $In_{0,1}Ga_{0,9}As$; curve 1 – same for films $In_{0,17}Ga_{0,83}As$.*

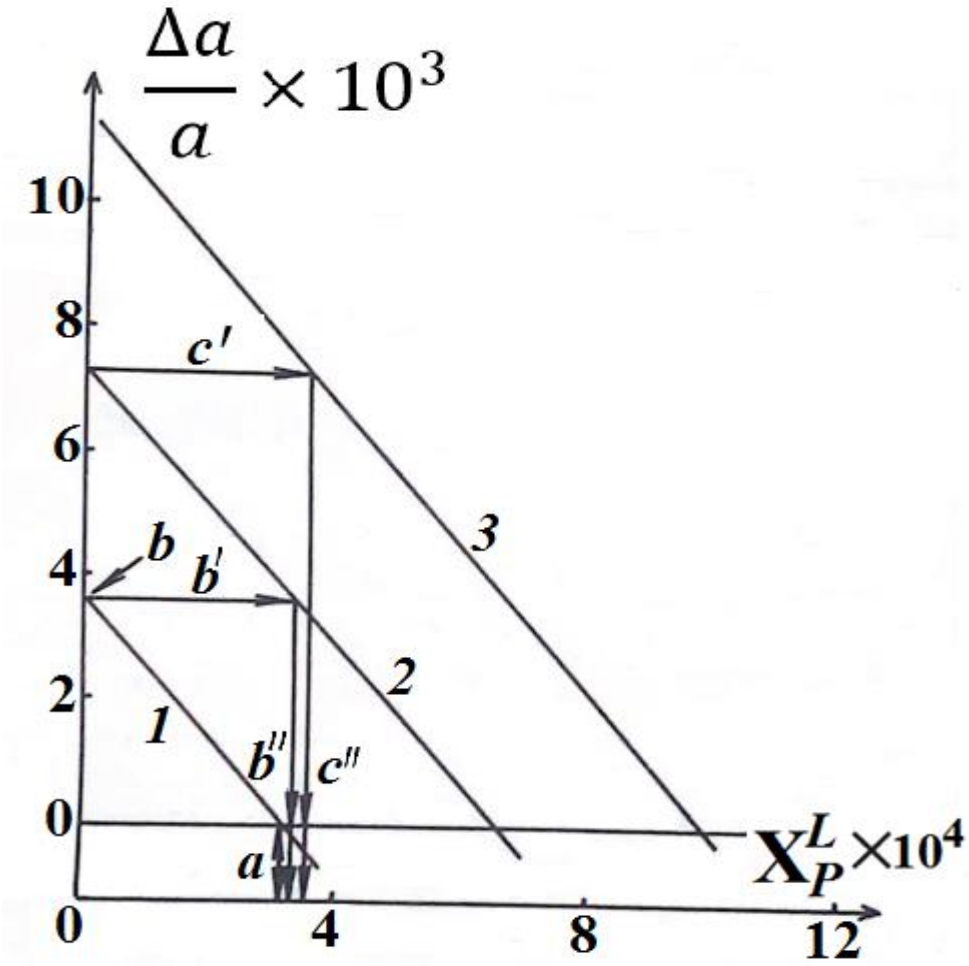


*Fig. 3. Relative deviation of the lattice parameter of the initial composition of the solid phazes $InGaAsP$ from $GaAs$ depending on the proportion of phosphorus in the liquid phase$In-Ga-As-P$ при 770 ℃ for: 1) composition $In_{0,05}Ga_{0,95}As/InGaAsP_{var}$ ; 2) $In_{0,1}Ga_{0,9}As/InGaAsP_{var}$ ; 3) $In_{0,17}Ga_{0,83}As/InGaAsP_{var}$ .*

Next, an even more narrow-gap film is grown $In_{0,17}Ga_{0,83}As$ from four-component liquid phase $In-Ga-As-P$, the composition of which for 770 ℃ selected in the same way: arrows $\boldsymbol{c'}$ and $\boldsymbol{c''}$ on Fig.3 and arrow $\boldsymbol{c}$ – on Fig.2. In this embodiment, a three-layer heterocomposite is obtained in a single process, with each layer grown in the temperature range 770 ℃ ÷ 700 ℃ (thickness of the solution layer on the substrate $l = 0{,}5\ mm$ and cooling rate $\alpha = 1$ ℃$/min.$, as earlier). It is clear that after the solution is displaced from the surface of the intermediate layer, the system must again heat up to 770 ℃ and maintained at this or higher ($\Delta T = 10 \div 20$ ℃) temperature to homogenize the next working solution. Films were obtained in this way $In_{0,17}Ga_{0,83}As$ (line copy of a microphotograph of a cleavage of such a structure - Fig. 4) with the density of threading dislocations, $N_D$, less $10^6\ sm^2$ on large area substrates ($S > 4\ sm^2$). In this case, the dislocation density was uniform over the area of the structure, with the exception of the edge sections of 1.5 mm.

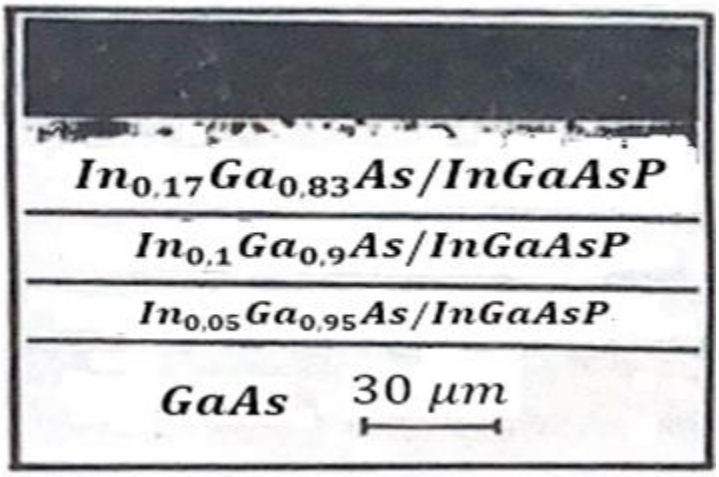


***Fig. 4. Line copy of a microphotograph of a cleavage of a three-layer heterocomposite $In_{0,17}Ga_{0,83}As/InGaAsP_{var}/In_{0,1}Ga_{0,9}As/InGaAsP_{var}/In_{0,05}Ga_{0,95}As/InGaAsP_{var}/GaAs$.***

The growth conditions we chose ensured that we obtained the indicated values. $N_D$ with a total thickness of the entire structure of 50÷70 μm (which reduced the bending of the entire composition), and also made it possible (surprisingly) to reduce the consumption of indium compared to the conventional single-layer version, when the thickness of the solution layer on the substrate is set equal to 3 mm in order to obtain an acceptable the magnitude of the composition gradient of the buffer layer.

There are also other options for obtaining heterostructures with films $In_xGa_{1-x}As$ ($x \geq 0.15$). For example, obtaining films with x≥0.15 through a two-layer heterocomposition of the type $In_{0,17}Ga_{0,83}As/InGaAsP_{var}/In_{0,08}Ga_{0,92}As/InGaAsP/GaAs$. The growth of this structure is carried out in a single process of sequential crystallization of the 1st layer – $In_{0,08}Ga_{0,92}As/InGaAsP_{var}$ (growth temperature range – 820 $^0$C÷770 $^0$C). Calculations of liquid phase compositions $In-Ga-As-P$ while similar to those described above. Further, it is possible to grow an additional layer of ternary solid solution $In_xGa_{1-x}As$ (third and fourth, depending on the type of composition), where it is possible to change the band gap $E_g$ within small limits, without compromising the structural perfection of the entire heterocomposition.

And finally, we should dwell on the situation when a “foreign” heterocomposition is used as a buffer layer of variable composition. For example, to obtain films $In_xGa_{1-x}As$ ($x \geq 0{,}15$)

smooth heterojunction can be used$GaAs_{1-y}Sb_y/GaAsSbP_{var}/GaAs$. Detailed methodology for the growth of graded-gap films $GaAs_{1-y}Sb_y/GaAsSbP_{var}/GaAs$ allowed us to grow from a thin layer of solution ($l = 0{,}5\ mm$) composition$y$~0,15 (on the surface) with dislocation density $N_D \leq 10^6\ sm^2$. In this composition range ($x$~0,17 для $In_xGa_{1-x}As$ and $y$~0,15 for $GaAs_{1-y}Sb_y$) lattice parameters $GaAs_{1-y}Sb_y$ и $In_xGa_{1-x}As$ are close, and it is possible to sequentially grow using the program cooling method $In_xGa_{1-x}As$ onto an epitaxial substrate$GaAs_{1-y}Sb_y$, without compromising the structural properties of the entire heterocomposition. However, in this case it is necessary to overcome the effects of such a factor as the instability of the nonequilibrium interface $GaAs_{1-y}Sb_y$ – saturated solution $In-Ga-As$. The experiment shows that if film growth $InGaAs$ preceded by contact with the epitaxial substrate $GaAsSb$ saturated solution $In-Ga-As$, then the interface of the resulting structure has the form shown in Fig. 5 $a$. There is evidence of corrosion of the substrate by the solution $In-Ga-As$ and subsequent recrystallization with the formation of defects of macroscopic sizes. This effect is suppressed by introducing supercooling of the liquid phase $In-Ga-As$, the value of which, ($\Delta T = 5\ K$ turns out to be sufficient for the formation of two-layer heterostructures with a uniform dislocation density over the area, the value of which is determined by the characteristics of the substrate used $GaAs_{1-y}Sb_y$ ($N_D \leq 10^6\ sm^2$, a copy of a microphotograph of a typical structure cleavage - in Fig. 5 B).

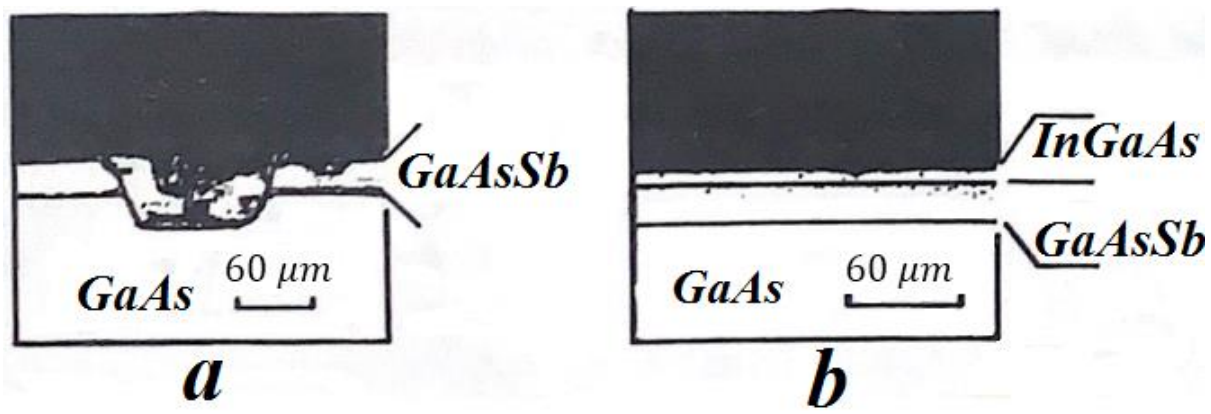


***Fig 5. Line copy of a microphotograph of a cleavage of a three-layer heterostructure type $In_{0,17}Ga_{0,83}As/GaAs_{1-y}Sb_y/GaAsSbP_{var}/Ga$:***
***a – with backing $GaAs_{1-y}Sb_y$ contacted saturated solution $In-Ga-As$;***
***б - solution $In-Ga-As$ before contact it was supercooled by 5 K.***

Thus, to obtain films of ternary solid solutions sufficiently distant in terms of the lattice parameter from the binary submarine $\frac{\Delta a}{a} \gtrsim 1\ \%$, It is possible to use multilayer heterocompositions with a fairly smooth change in composition along the thickness without any fundamental difficulties.

During heteroepitaxial growth of films, two factors are significant: a) chemical mismatch between the film and the substrate, due to the difference in the compositions of the conjugating phases, and b) structural mismatch, characterized by the difference in the lattice and substrate parameters at the growth temperature. A large chemical mismatch can cause the formation of three-dimensional centers of a new phase at the initial stage of film growth, depending on the situation created in the near-surface region of the substrate—the separating layer.

Structural mismatch leads to the appearance of stress both in the film system and at an earlier stage of the process - at the stage of contact of the liquid and solid phases - in the separating layer. The existence of these stresses has a noticeable effect on all stages of the film formation process: on the conditions of quasi-equilibrium liquid phase/substrate, the formation of centers of a new phase and the preferential growth mechanism of the first continuous layer of the film, on the structural perfection and morphology of the film, as well as on the nature of the transition layer substrate.

Two different mechanisms of formation of the separating layer at the liquid/solid phase interface - epitaxial and often diffusion - are undoubtedly genetically responsible for the size and nature of the transition layer observed in specific heterostructures.

Knowledge of the features and patterns of the initial stages of heteroepitaxial growth of films from the liquid phase will make it possible to more fully reveal the capabilities of modern LPE technology in obtaining ultrathin (about 10 nm) heterolayers necessary for new generation devices.

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