

Research Article

Structural Studies of the Epitaxial Layer of a Substitutional Solid Solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ with Nanocrystals

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In this work, we explored the possibility of growing a substitutional solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ with an ordered array of nanosize crystals on GaAs (100) substrates. Grown epitaxial films were investigated by the X-ray diffraction analysis method. The chemical composition of the grown epitaxial films was determined by a X-ray microanalyzer, along the thickness of the epitaxial layer. The photoluminescence spectrum was studied and a peak is observed at $\lambda_{\text{max}} = 465$ nm, corresponding to the width of the band gap of zinc selenide $E_{\text{ZnSe}} = 2.67$ eV, which is apparently due to the nanocrystals ZnSe, disposed in the surface region of the epitaxial film of a solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$. Size of nanocrystals were evaluated by an atomic force microscopy.

1. Introduction

The processes of self-organization during the growth of epitaxial films play an important role.

A qualitative breakthrough in the field of obtaining semiconductor nanostructures is associated with the effect of self-organization of semiconductor nanostructures in heteroepitaxial semiconductor systems. The spontaneous appearance of periodically ordered structures on the surface and in epitaxial films of semiconductors covers a wide range of phenomena in solid state physics and in semiconductor technology [1]. The appearance of ordered arrays of quantum dots due to the effect of self-organization plays an important role in the creation of devices working on the basis of size effects.

Since the lattice parameter of the GaAs compound ($a_{\text{GaAs}} = 5.6532$ Å) and ZnSe ($a_{\text{ZnSe}} = 5.6676$ Å) has close values and they have the same crystalline structure (zinc blende), these compounds are promising materials for obtaining high quality ZnSe/GaAs heterostructures and substitutional solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$. The quality of such heterostructures is one of the key moments for manufacturing optoelectronic devices, such as lasers and light-emitting diodes. In addition to its technological value, the ZnSe/GaAs heterostructure is a model system for investigating many

fundamental aspects of surface and interfaces II-VI/III-V. However, such an interface has a complex character with respect to stoichiometry and its chemical reactivity. In Reference [2], ZnSe-GaAs heterovalent heterostructures were fabricated by metalorganic vapour-phase epitaxy and characterized structurally and electrically. Authors successfully fabricated quantum-well structures and GaAs islands buried into ZnSe. Funato et al. had investigated MOVPE growth procedures of GaAs/ZnSe heterostructures, the ZnSe-GaAs heterovalent quantum structures were fabricated, and their optical properties were characterized [3]. Farrell and LaViolette studied [4] three categories of simple heterojunctions that have links: (1) only As-Zn, (2) only Se-Ga, and (3) mixed As-Zn and Se-Ga bonds and more complex interface configurations, as well as various versions of interfacial stoichiometry [5]. He showed that the energy of the interface can be expressed as a simple sum of the energies of pairs with one bond, with an average error of less than 3%. X-ray diffraction analysis showed that sequential annealing of the relaxed layer of ZnSe, grown on GaAs (001) by molecular beam epitaxy, leads to migration of Ga toward ZnSe, with a significant accumulation of As atoms near the ZnSe. At the boundary region of the heterostructure, the Ga_2Se_3 compound is formed as a by-product, whereas the Zn atoms diffuse from the interface into the GaAs substrate [6]. In Reference [7], the possibility of growing of the

variable-gap solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, by liquid-phase epitaxy from a Pb solution-melt on GaAs (100) substrates with a diameter of 20 mm, in the temperature range 870–730°C, was demonstrated. Epitaxial layers $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ had an n -type conductivity, a carrier concentration of $n = 7.6 \cdot 10^{19} \text{ cm}^{-3}$, and a monocrystalline structure with a continuously varying composition x from 0 to 0.07.

In Reference [8], on the basis of calculations of pseudo-potential flat waves, it has been shown that the enthalpy of formation and length of covalent bond Zn-Se ($R_{\text{Zn-Se}}$) in the material GaAs depend on the atoms surrounding it. Taking into account that, in the usual ZnSe value of covalent bond, $R_{\text{Zn-Se}} = 2.42 \text{ \AA}$, it was shown that, in a tetrahedral lattice of GaAs when the impure Zn atom is surrounded with 4 Se atoms, i.e., in the cluster Zn-Se₄, its value makes $R_{\text{Zn-Se}} = 2.44 \text{ \AA}$; in the cluster of Zn-Se₃As, $R_{\text{Zn-Se}} = 2.46 \text{ \AA}$; in the cluster of Zn-Se₂As₂, $R_{\text{Zn-Se}} = 2.49 \text{ \AA}$; and in the cluster of Zn-SeAs₃, $R_{\text{Zn-Se}} = 2.51 \text{ \AA}$. The similar situation is observed when impure Se atom in GaAs is surrounded with Zn atoms. The more the length of the Zn-Se bond, the more it is surrounded with GaAs atoms, both for cationic and for anionic knot. On the basis of experimental data in the paper [9], the extrapolation dependence of width of the forbidden zone of solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($E_{g, \text{GaAsZnSe}}$) from concentration ZnSe (x) is shown at the room temperature: $E_{g, \text{GaAsZnSe}} = 1.43 - 0.09x + 1.26x^2$ (eV) ($0 \leq x \leq 1$). Within change of concentration of ZnSe from 0 to 10% ($0 \leq x \leq 0.1$), change of $E_{g, \text{GaAsZnSe}}$ makes no more than 0.25%, i.e., practically does not change. It is caused by a low possibility of a clustering of Zn + Se in GaAs.

In this paper, the appearance of spontaneous formation of ordered arrays of nanoscale crystals on the surface of epitaxial film of a solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ has been studied. Since the process of liquid-phase epitaxy is carried out under conditions very close to equilibrium ones, the phenomenon of self-organization plays an important role during the liquid-phase epitaxy.

2. Theory and Calculation

To elucidate the possibility of formation of a substitutional solid solution for GaAs and ZnSe semiconductor compounds, we start from the thermodynamic principle of crystal chemistry, which consists in the fact that, in any physical and chemical system with chemical components, there is a chemical interaction between atoms (or ions) for all their quantitative ratios. Molecular elements III–V and II–VI, which do not appear on traditional state diagrams in the form of compounds, are considered as new chemical compounds, which as components of the system participate in the formation of solid solutions. Under certain thermodynamic conditions, the possibility of forming a substitutional solid solution by molecules of semiconductor compounds is determined by the type of crystal lattices of the constituent components, their charge states, and geometric dimensions. Taking into account these factors and the possibility of replacing two, three, or four nearest neighboring atoms of the solvent A , respectively, with two-, three-, or four-atom molecules of soluble compound D , the conditions for the

formation of a substitutional solid solution in the following forms were proposed in [10]:

$$\Delta z = \sum_{S=A} z_s - \sum_{i=D} z_i = 0, \quad (1)$$

$$|\Delta r| = \left| \sum_{S=A} r_s - \sum_{i=D} r_i \right| \leq 0.1 \cdot \sum_{S=A} r_i, \quad (2)$$

where z_s and z_i are the valence and r_s and r_i are the covalent radiuses of the atoms of solvent A and the soluble D chemical element or elements forming molecules of solvent A and soluble D compounds, respectively, $i = 1, 2, 3, 4$. Condition (1) provides for the electroneutrality of soluble chemical elements or compounds in a solvent semiconductor material; it is performed when the soluble elements are izovalent to the solvent semiconductor. Condition (2) provides for the proximity of the geometric parameters of the solvent A and the soluble D compound, which preclude the appearance of significant distortions of the crystal lattice in solid solutions. The smaller Δr , the smaller the energy of the elastic distortions of the crystal lattice, therefore the greater the crystal perfection of the substitutional solid solution and the greater the solubility of D in A . When the difference in the sum of the covalent radiuses of the atoms of the molecules is greater than 10%, the formation of a substitutional solid solution of these components is insignificant.

For diatomic molecules of semiconductor compounds III–V and II–VI, conditions (1) and (2) have the following forms:

$$\Delta z = (z_{\text{III}} + z_{\text{V}}) - (z_{\text{II}} + z_{\text{VI}}) = 0, \quad (3)$$

$$\Delta r = |(r_{\text{III}} + r_{\text{V}}) - (r_{\text{II}} + r_{\text{VI}})| \leq 0.1 \cdot (r_{\text{III}} + r_{\text{V}}), \quad (4)$$

$$\Delta r = |(r_{\text{III}} + r_{\text{V}}) - (r_{\text{II}} + r_{\text{VI}})| \leq 0.1 \cdot (r_{\text{II}} + r_{\text{VI}}),$$

where z_{II} , z_{III} , z_{V} , and z_{VI} are the valencies and r_{II} , r_{III} , r_{V} , and r_{VI} are the covalent radiuses of the elements of groups II, III, V, and VI, respectively. Since for the GaAs molecules, $z_{\text{Ga}} + z_{\text{As}} = 3 + 5 = 8$ and $r_{\text{Ga}} + r_{\text{As}} = 2.43 \text{ \AA}$ and for ZnSe, $z_{\text{Zn}} + z_{\text{Se}} = 2 + 6 = 8$ and $r_{\text{Zn}} + r_{\text{Se}} = 2.45 \text{ \AA}$, then, conditions (3) and (4) are satisfied. Since the difference in the sum of the covalent radiuses of the atoms of the GaAs and ZnSe molecules is $\sim 0.4\%$ and the difference in the lattice parameters of the GaAs and ZnSe binary compounds is less than 0.3%, the mutual molecular substitution of these components does not strongly deform the crystal lattice. When the GaAs molecules are replaced by ZnSe molecules, the energy of elastic distortions of the crystal lattice will be minimal; therefore, they form a continuous substitutional solid solution in the form $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ in the entire range of compositions $0 \leq x \leq 1$. The tetrahedral bonds of such a solid solution are shown in Figure 1. Figure 1(a) shows the tetrahedral bonds in a $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ layer, enriched with gallium arsenide, when some of the molecules in the GaAs matrix are replaced by the ZnSe molecule, and Figure 1(b) shows a layer enriched with ZnSe, when some molecules in the ZnSe matrix are replaced by GaAs molecules.

Solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ was grown on single-crystal GaAs substrates with an orientation (100), p -, and n - type

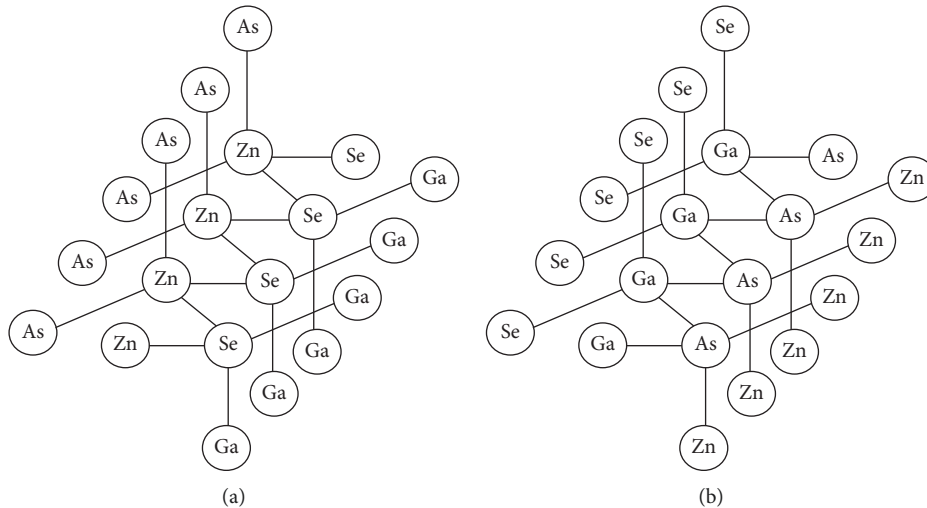


FIGURE 1: Tetrahedral bonds of the substitutional solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ in layers enriched with gallium arsenide (a) and zinc selenide (b).

conductivity ($p = 5 \times 10^{18} \text{ cm}^{-3}$, $n = 3 \times 10^{17} \text{ cm}^{-3}$) by liquid-phase epitaxy, according to the technology described in [11]. The substrates had a diameter of 20 mm and a thickness of $\sim 400 \mu\text{m}$. To grow the layers, we used a vertical type quartz reactor with horizontally arranged substrates. The growth of the epitaxial layer was realized from a small volume of a tin solution-melt, bounded by two substrates in an atmosphere of hydrogen, purified by palladium (Figure 2), which made it possible to minimize the amount of the consumable solution-melt. First, a vacuum was created in the reactor to a residual pressure of 10^{-2} atmosphere, then purified hydrogen was passed through the reactor for 15 min, and then, the heating process began. When the temperature reached the required value, the system switched to the automatic mode. During 50–60 min, the solution-melt was homogenized. Then, the substrates on the graphite holder were brought into contact with the solution-melt and after filling the gaps between the substrates with solution-melt, graphite holder was raised 1 cm above the solution level.

For the preparation of a solution-melt, the solubility of GaAs and ZnSe in Sn, in the temperature range $720\text{--}650^\circ\text{C}$, was studied by the method of weight loss of samples of gallium arsenide and zinc selenide, placed in liquid tin and held in it until the solution saturation. Figures 3 and 4 show data on the solubility of GaAs and ZnSe in tin as a function of temperature. Data for GaAs are taken from the work of the authors [12] and for ZnSe, from the work of Kumar [13].

The composition of the Sn-GaAs-ZnSe solution-melt at 720°C was as follows: Sn: 100 g, GaAs: 2.54 g, and ZnSe: 0.25 g.

We assume that the dissolved compounds GaAs and ZnSe in liquid tin at a temperature of liquid-phase epitaxy (720°C) are mainly in the form of molecules GaAs and ZnSe. This assumption is based on an analysis of the solubility of ZnSe and GaAs in Sn. The decomposition of ZnSe molecules, when dissolved in Sn, into individual Zn and Se atoms, according to the state diagram of the alloys, is equivalent to the simultaneous dissolution of Zn and Se in Sn. As is

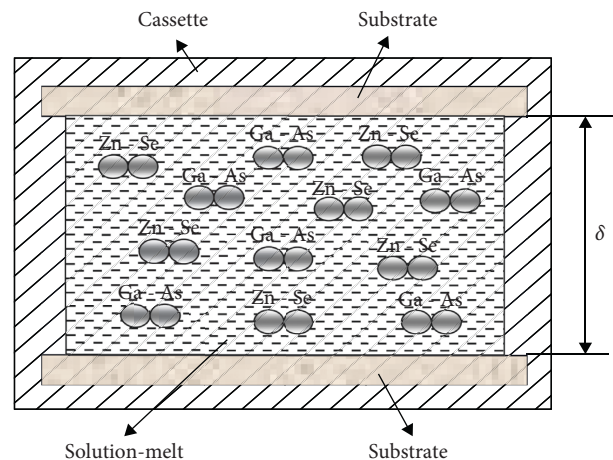


FIGURE 2: Diagram of a graphite cassette with horizontally placed substrates and a solution-melt (the thickness of the gap between the substrates is $\delta = 1 \text{ mm}$).

known, all these three substances Zn, Se, and Sn at a temperature of 720°C are in a molten state (as their melting points are below 720°C) and have unlimited solubility among themselves.

Consequently, if the ZnSe molecules decompose into individual Zn and Se atoms when ZnSe is dissolved in Sn, the solubility of ZnSe in Sn should be unlimited at 720°C . It is known that the solubility of ZnSe in Sn is very limited, and is only 0.3 mole % at 720°C [13], which indicates that the dissolved ZnSe in the tin solution-melt is mainly in the form of ZnSe molecules.

In addition, one of the main conditions of liquid-phase epitaxy is that the solution-melt must be supersaturated. If the ZnSe molecules in Sn decompose into individual Zn and Se atoms, then at a content of 0.3 mole % ZnSe in Sn at 720°C , the solution-melt, according to the state diagram of the alloys, will not be supersaturated with zinc and selenium, and the epitaxial growth of ZnSe does not occur. The fact

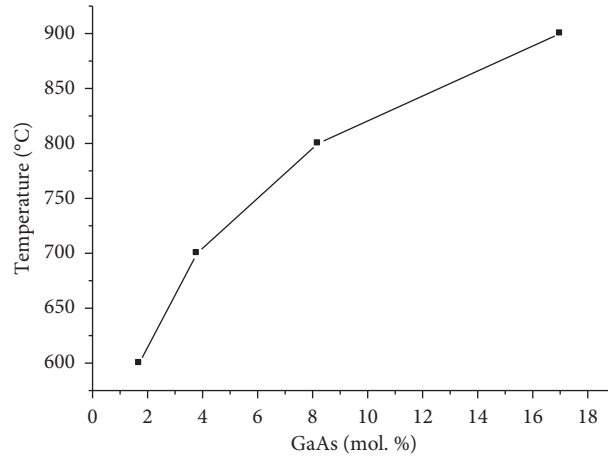


FIGURE 3: Dependence of the solubility of GaAs in Sn on temperature.

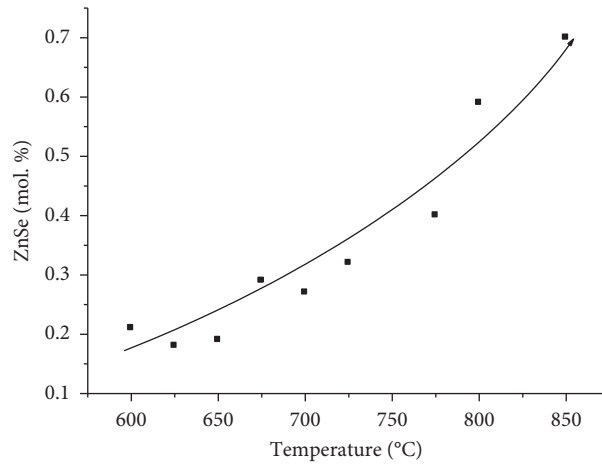


FIGURE 4: Dependence of the solubility of ZnSe in Sn on temperature [9].

that under these conditions the epitaxial growth of ZnSe is observed indicates that the tin solution-melt is saturated with ZnSe molecules and that the ZnSe molecules do not decompose into individual Zn and Se atoms.

The same conclusions can be drawn for GaAs, dissolved in Sn.

Therefore, we assume that GaAs and ZnSe in tin solution-melt are mainly in the form of GaAs and ZnSe molecules (Figure 2).

Since the sum of the covalent radii of the atoms of the GaAs molecules ($r_{\text{Ga}} + r_{\text{As}} = 2.43 \text{ \AA}$) and ZnSe ($r_{\text{Zn}} + r_{\text{Se}} = 2.45 \text{ \AA}$) is close and the sum of the valencies of their atoms is equal ($z_{\text{Ga}} + z_{\text{As}} = z_{\text{Zn}} + z_{\text{Se}}$), then the substitution of diatomic molecules at the crystal lattice sites of the solid solution is energetically more favorable than the atomic substitution of the crystal lattice site by Ga, As, Zn, or Se atoms separately.

Based on the principle of similarity, that is, similar dissolves in like, it can be assumed that, at the initial moment of growth of the epitaxial layer, crystallization of gallium arsenide layers occurs since at a chosen epitaxy temperature the solution is saturated by GaAs. At lower temperatures, conditions are created for the growth of the $(\text{GaAs})_{1-x}(\text{ZnSe})_x$

solid solution, since at these temperatures the solution-melt on the crystallization front becomes supersaturated by gallium arsenide and zinc selenide. Samples were grown at various values of liquid-phase epitaxy parameters. The distance between the upper and lower substrates (δ) and the beginning and the end of the crystallization temperature (T) and the rate of forced cooling of the tin solution-melt (v) were varied.

The epitaxial layers studied in this work were obtained at a distance between the upper and lower substrates $\delta = 1 \text{ mm}$, the temperature of the beginning of crystallization $T = 700^\circ\text{C}$, the crystallization termination temperature $T = 650^\circ\text{C}$, and the cooling rate $v = 1^\circ\text{C}/\text{min}$. The thickness of the grown films was 4 micron. The grown films had a hole type of conductivity. Some electrophysical parameters were determined by the Hall method.

At room temperature, the resistivity of epitaxial layers was $\rho = 0.18 \text{ Ohm}\cdot\text{cm}$, the Hall mobility was $\mu = 60 \text{ cm}^2/(\text{V}\cdot\text{s})$, and the concentration of the main carriers was $p = 2 \times 10^{18} \text{ cm}^{-3}$.

The density of dislocations at the interface is $N = 10^7 \text{ cm}^{-2}$ and on the surface of the epitaxial film is $N = 4 \times 10^5 \text{ cm}^{-2}$. To determine the density of dislocations, the surface of the

epitaxial film was etched with a selective etchant $\text{HNO}_3 : \text{H}_2\text{O}$ (1 : 1), for 2–4 minutes; then, the dislocations were examined with a microscope MIM-4. The width of the band gap on the surface of the epitaxial film, where the composition of the solid solution $(\text{GaAs})_{0.96}(\text{ZnSe})_{0.04}$ is $E_g = 1.46$ eV.

3. Structural Studies of a Solid Solution

$(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.80$)

Structural studies of a GaAs substrate and an epitaxial film $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ were performed at 300 K on the X-ray diffractometer DRON-3M (CuK α radiation, $\lambda = 0.15418$ nm) on scheme θ - 2θ in the step scanning mode.

Figure 5 shows the X-ray diffraction pattern of a single-crystal GaAs substrate. It can be seen that, in the diffraction pattern, there are several structural reflexes of selective nature with a very large and hardly noticeable intensity at the nonmonotonic background level. The analysis showed that the substrate surface corresponds to the crystallographic plane (100). This is evidenced by the presence on the roentgenogram of a series of selective reflexes H00 (where $H = 1, 2, 3, \dots$), intense lines $(200)_{\text{GaAs}}$ with $d/n = 0.2822$ and $(400)_{\text{GaAs}}$ with $d/n = 0.1412$ nm. Their β components are visible at scattering angles, $2\theta = 28.5^\circ$ and $2\theta = 58.4^\circ$, respectively. The narrow width (FWHM = 0.0019 rad), the maximum intensity ($4 \cdot 10^5$ imp.sec $^{-1}$), and the good splitting of the $(400)_{\text{GaAs}}$ reflex by α_1 and α_2 radiation with the ratio of the intensities of the components close to the calculated ones, $I(\alpha_1) = 2 \cdot I(\alpha_2)$ (Figure 5, inset) indicate the perfection of the crystal lattice of the substrate. The background level has a nonmonotonic character, the steps are clearly distinguished (in the figure, they are shown by arrows) at the background level on both sides of the structural reflex $(200)_{\text{GaAs}}$ and near the [200] direction at $2\theta = 33.6^\circ$, there is a wide diffuse reflection (FWHM = 0.2 rad). The analysis showed that diffuse scattering is due to disordered structural fragments with a characteristic size $L_d \approx 7.8$ Å. The features of the arrangement of the steps in the X-ray diffraction pattern, almost equal to the distance from the selective reflex $(200)_{\text{GaAs}}$ to each of them, suggest that the steps are satellites of the structural line $(200)_{\text{GaAs}}$. The satellites indicate a periodic arrangement of structural fragments that cause diffuse scattering at $2\theta = 33.6^\circ$ around the direction (200), that is, the substrate structure is modulated. Since the lattice of the substrate is cubic (a sphalerite-type lattice), the modulation period can be determined from the angular distance $\Delta\theta$ (in radians) between the satellite and the main reflection maximum (HKL) on the X-ray diffraction diagram using the formula $S = a \cdot H \cdot \text{tg}\theta / [(H^2 + K^2 + L^2) \cdot \Delta\theta]$, where θ is the scattering angle and a is the lattice constant of the substrate [14]. For a given substrate, $S \approx 16.3$ Å, that is, $S \approx 2 \cdot L_d$.

Figure 6 shows X-ray diffraction of the epitaxial film of the solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.80$). The X-ray diffraction pattern of the grown epitaxial film was significantly different from the X-ray diffraction pattern of the substrate. While maintaining nonmonotonicity background, its level in the film as compared with the background level of the substrate in small scattering angles fell to 5% and in medium and high angles increased by 70 and 80%, respectively. Also,

the intensity of the main reflections $(200)_{\text{GaAs}}$ and $(400)_{\text{GaAs}}$ increased by 5% and 20%, respectively; and the ratio of the intensity with respect to the α_1 and α_2 radiation of the reflex $(400)_{\text{GaAs}}$ changed and became $I(\alpha_1) \neq 2 I(\alpha_2)$ (Figure 6, insert); the steps were smoothed from the side of small scattering angles (Figure 6). All this indicates that the surface of the substrate is covered with a film of appreciable thickness. The absence of other structural reflections in the roentgenogram shows the coincidence of the orientation of the film with the orientation of the substrate, that is (100). The increase in the intensity of the main reflections $(200)_{\text{GaAs}}$ and $(400)_{\text{GaAs}}$ and the level of the inelastic background, beginning with the mean scattering angles, can be explained by the difference in the electronic structure and elemental composition of the film and substrate. As is known, X-rays are scattered by the electrons of the ions of the material [14]. Apart from the number of electrons in the filled inner shells in the GaAs system, the number of generalized valence electrons in the p -state is 4 units ($4p^1$ and $4p^3$ states of Ga and As, respectively). In the case of ZnSe, the number of generalized electrons as a result of sp hybridization of external orbital reaches up to 6 units. If some molecules in the GaAs matrix are replaced by the ZnSe molecule or the grown film has the composition $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, then this leads to an increase in the intensity of the main reflexes of the H00 type. The change in the level of the inelastic background at the middle and far scattering angles is also the result of the introduction of ZnSe molecules into the GaAs matrix, since, in the roentgenogram, the minimum level of the inelastic background is reached under the condition $Z_{\text{spl}} > Z_{\text{anod}}$ [15]. In our case, CuK α -radiation of a copper anode is used. In the composition of the film, there is an element Zn, which in the periodic system is next to copper. This leads to a noticeable increase in the inelastic X-ray scattering cross section for the electrons of the material's ions, which results in an increase in the background level in the X-ray diffraction pattern. In addition, there is a significant difference in the parameters of the film and substrate lattice. The parameters of the crystal lattice of the film and substrate perpendicular to the plane of the layer were determined from the $(200)_{\text{GaAs}}$ and $(400)_{\text{GaAs}}$ structural lines using the Nelson-Riley $1/2((\cos^2 \theta)/(\sin \theta) + (\cos^2 \theta)/\theta)$ extrapolated to $\theta = 90^\circ$ [16]. The lattice parameters of the film (a_f) and the substrate (a_s) were $a_f = 5.6544$ and $a_s = 5.6465$ Å, respectively. The mismatch of the lattice constants $\xi = 2|a_s - a_f|/(a_s + a_f) = 0.0014$. The accuracy of determining the interplanar distances and lattice parameters was ~ 0.0001 Å. Thus, the grown epitaxial film is a single crystal of the substitutional solid solution in the form $(\text{GaAs})_{1-x}(\text{ZnSe})_x$.

3.1. X-ray Microprobe Analysis of the Chemical Composition of the Solid Solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.80$).

Studies of the chemical composition of the grown epitaxial layers $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ were carried out on the X-ray microanalyzer "Jeol" JSM 5910 LV-Japan. Based on the results of the X-ray microprobe analysis, the distribution profile of Ga, As, Zn, and Se atoms was determined as a

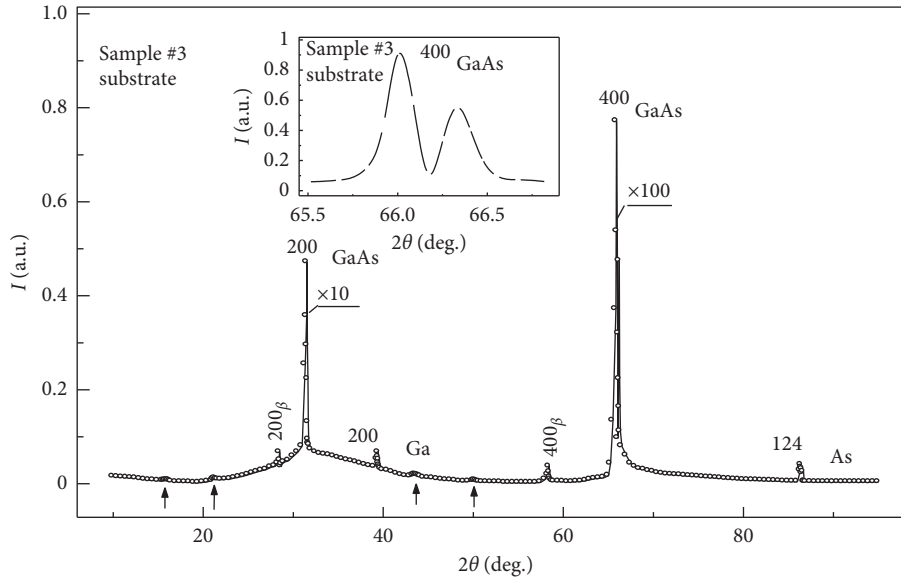


FIGURE 5: The X-ray diffraction pattern of the GaAs substrate.

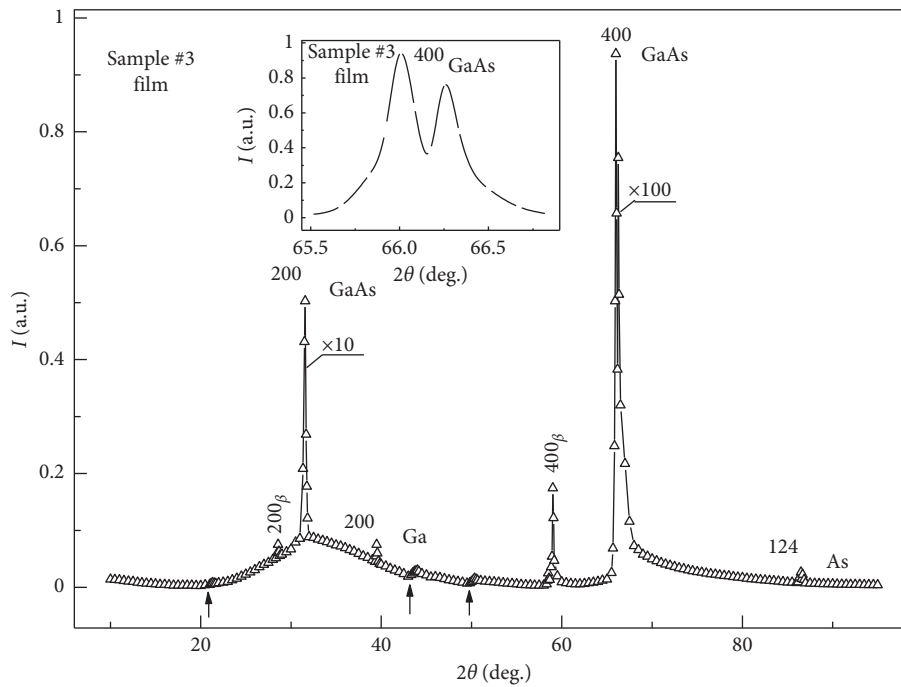


FIGURE 6: X-ray diffraction pattern of epitaxial film of solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.80$).

function of the depth of the epitaxial layer (Figure 7). Figure 7 shows that, with the growth of the solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, the molar ZnSe content in the epitaxial layer first increases rapidly, reaching a maximum value of $x = 0.80$, which is probably due to the high supersaturation of the solution-melt on the crystallization front by zinc selenide. Further, the molar content of ZnSe slowly decreases, reaching the value $x = 0.04$ on the near-surface region of the film.

Since the growth of the epitaxial layer is carried out from a limited volume of the solution-melt and since the solubility of ZnSe is 10 times lower than the solubility of GaAs in tin, then after the intensive introduction of zinc selenide into the solid

phase, the solution-melt is depleted with ZnSe, which further causes a gradual decrease in the molar content of ZnSe in the direction of growth. At a depth of $2 \mu\text{m}$ from the surface of the film, the molar content of ZnSe does not exceed 10%. Thus, the grown film is a substitutional solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.80$) with a gradually varying composition. A wide-band layer, enriched with ZnSe, is formed between the substrate and the near-surface region of the film.

3.2. Investigation of the Surface of Epitaxial Films $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.04$). The surface of the epitaxial

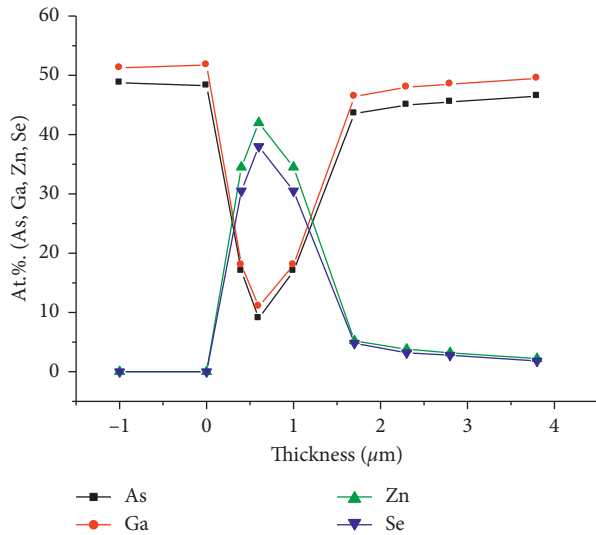


FIGURE 7: The distribution profiles of Ga, As, Zn, and Se atoms in the epitaxial layer of the solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$.

film was investigated by using an atomic force microscope. Figures 8 and 9 show two-dimensional and three-dimensional images of the surface of epitaxial films, respectively. From Figures 8 and 9, it can be seen that, on a smooth surface of an epitaxial film, a series of “hillocks” with a base diameter up to ~ 300 nm and a height up to ~ 18 nm are formed.

Figure 10 represents the linear dimensions of the “hillocks” corresponding to the indicated points 1, 2, and 3 in Figure 8 and in Figure 11, the linear dimensions correspond to points 4, 5, and 6 in Figure 8. Analysis shows that the roughness of the smooth part of the surface does not exceed ~ 1 nm. In the diffractogram of the epitaxial film, intensive narrow structural reflections (200) and (400) were present, the absence of other structural reflexes and diffuse reflection indicate that the images of the “hillocks,” present on the AFM, seem to be nanocrystals with orientation (100), and they are arranged coherently with the matrix of the crystal lattice of the solid solution.

3.3. Photoluminescence of the Epitaxial Layer of the Solid Solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ ($0 \leq x \leq 0.80$). In Figure 12, the photoluminescence spectrum (PL) of the surface of the epitaxial layer $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ is given. PL excitation was carried out by laser radiation ($\lambda_{\text{laser}} = 325$ nm) from the side of the epitaxial layer at the temperature of liquid helium (5 K); the signal was recorded at the SDL-2 facility. As can be seen from Figure 12, the PL spectrum of the solid solution has a broadband covering almost the whole visible radiation spectrum range from 400 to 760 nm with a narrow emission peak at $\lambda_{\text{max}} = 465$ nm, corresponding to the width of the forbidden band of zinc selenide $E_{\text{ZnSe}} = 2.67$ eV.

Since the supplied laser radiation with energy of 3.82 eV is almost completely absorbed in the near-surface region of the epitaxial layer with a thickness of ~ 1 μm , the luminescent radiation comes from the film sublayer, where the molar ZnSe content is ~ 4 -5 mol%.

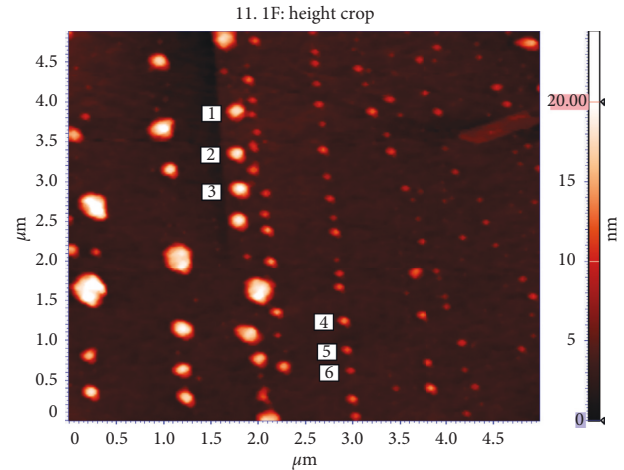


FIGURE 8: Two-dimensional image of the surface of an epitaxial film of a solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, obtained by using an atomic force microscope.

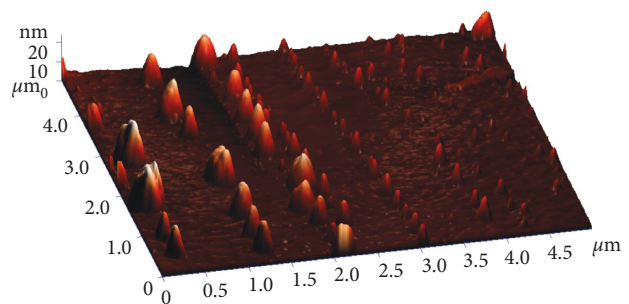


FIGURE 9: Three-dimensional image of the surface of an epitaxial film of a solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, obtained by using an atomic force microscope.

The appearance of a narrow peak in the PL spectrum at 465 nm, corresponding to the width of the band gap of zinc selenide $E_{\text{ZnSe}} = 2.67$ eV, although the molar content of ZnSe in the layer from which the luminescence occurs is only ~ 4.5 mol%, apparently indicates that the “tubercles” in Figure 9 are nanocrystals consisting of ZnSe.

The appearance of ZnSe nanocrystals in the matrix of the solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ is the result of the process of self-organization during the epitaxial growth of the film from the liquid-phase of a limited volume of the tin solution-melt (GaAs-ZnSe-Sn) .

At the liquid-phase growing solid solutions of $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ with ZnSe nanocrystals, due to the lattice parameter of the GaAs and ZnSe compounds differ by only 0.1%, the obtained epitaxial film is almost perfect, without microstresses in the crystal lattice.

4. Conclusions

Thus, in this paper, the possibility of forming an ordered array of nanoscale crystals in the near-surface region of the epitaxial film of the substitutional solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, during growing from the liquid phase,

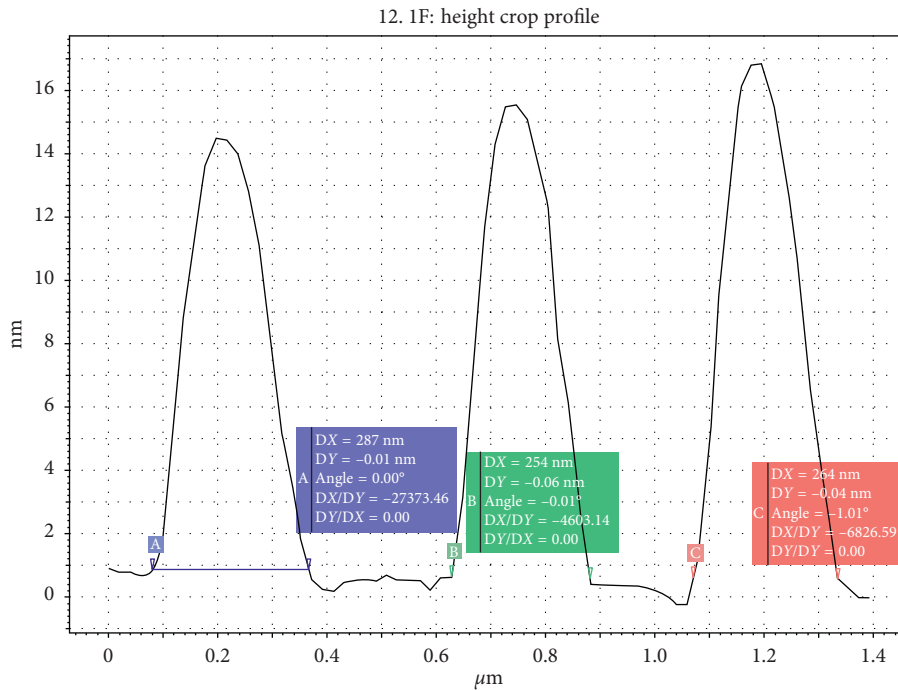


FIGURE 10: The linear dimensions of the “hillocks” corresponding to the indicated points 1, 2 and 3 in Figure 8.

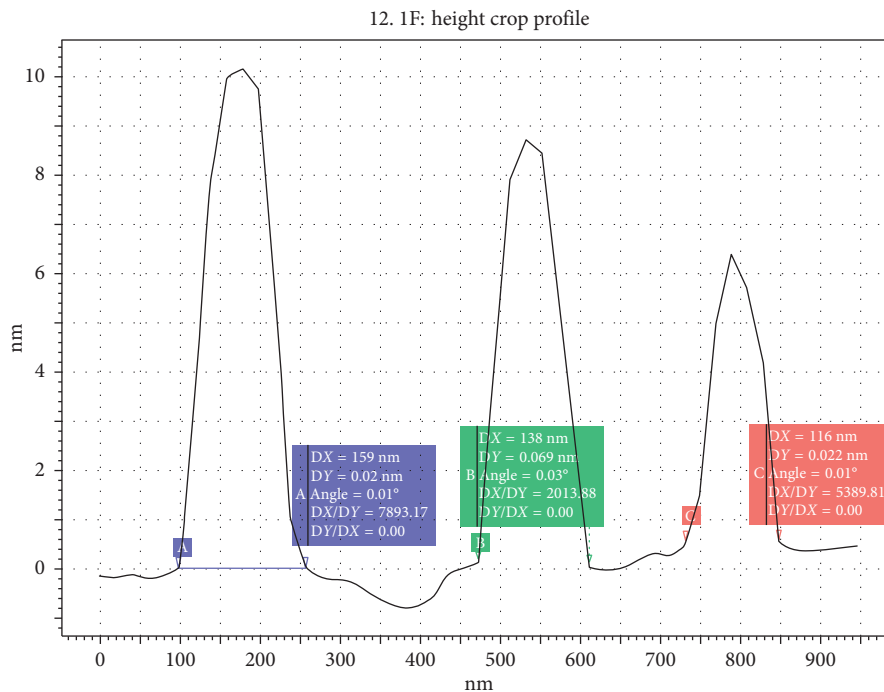


FIGURE 11: The linear dimensions of the “hillocks” corresponding to the indicated points 4, 5, and 6 in Figure 8.

due to self-organization processes, is shown. Studying of regularities of formation of the ordered multitude of nanoscale crystals in volume or on the surface of the other basic material gives the opportunity of operation of the sizes of nanocrystals, to manufacture the devices working

on the basis of size effect and to broaden the range of spectral sensitivity of basic material. ZnSe nanocrystals in the matrix of GaAs form the localized levels in the band gap of the solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$ at $E_i = 2.67 \text{ eV}$, that lead to expansion of that spectral range of

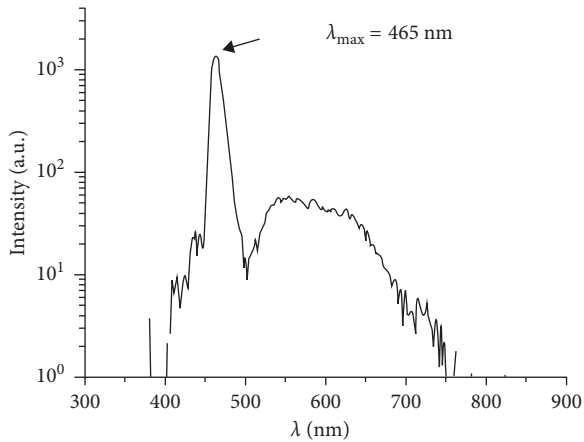


FIGURE 12: The photoluminescence spectrum of epitaxial layer of the solid solution $(\text{GaAs})_{1-x}(\text{ZnSe})_x$, at a temperature of 5 K.

photosensitivity of devices to high photon energy on their basis, as it is usually observed in structures with quantum dots.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

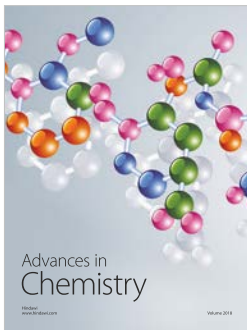
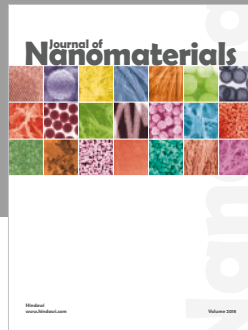
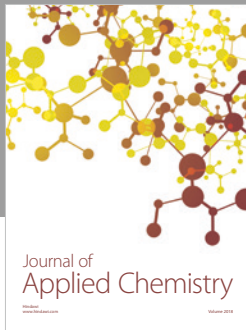
Acknowledgments

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