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GROWTH AND INVESTIGATION OF THE (GAAS)_{1-x-y}(GE)_x(ZNSE)_y SEMICONDUCTOR ALLOY

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In this article, the experimental and theoretical studies on technology for producing the single-crystal semiconductor alloy (GaAs)_{1-x-y}(Ge)_x(ZnSe)_y on GaAs substrates with the crystallographic orientation (100) by the liquid-phase epitaxy method is presented. The optimal process conditions of structurally perfect epitaxial layers were determined (cooling rate is 1°C/min, temperature is 730–640°C, and growth rate ϑ = 0.15 μm/min). The grown epitaxial films possessed thickness values of 10 μm and p-type conductivity with resistivities 0.1 Ω cm and the concentration of carriers 5.1·10^{17} cm^{-3}.

Keywords: substrate, film, liquid-phase epitaxy, semiconductor alloy, single-crystal, solid solutions.

The processes of self-organization during the growth of epitaxial films play an important role. Breakthrough in the fabrication of semiconductor nanostructures is related to the self-organization of semiconductor nanostructures in heteroepitaxial semiconductor systems. The spontaneous appearance of periodically ordered structures on surface and epitaxial semiconductor films involves a broad range of phenomena in the physics of solid state and semiconductor technology. It appearance of ordered quantum dotmassives due to the self-organization effect plays an important role in the development of the devices operating on the basis of size effects. Because the lattice parameters of Ge (a_{Ge} = 0.5657 nm) and GaAs (a_{GaAs} = 0.5653 nm) and ZnSe compounds (a_{ZnSe} = 0.5667 nm) [1] are similar and they possess identical crystal structure (sphalerite), these compounds are promising materials for the fabrication of high-quality Ge/ZnSe/GaAs heterostructures and continuous (GaAs)_{1-x-y}(Ge)_x(ZnSe)_y, (Ge)_x(ZnSe)_y, and (Ge)_x(GaAs)_y(ZnSe)_z substitutional solid solutions [1]. The quality of these heterostructures is one of the key points for the fabrication of optoelectronic devices, such as lasers and light-emitting diodes. In addition to process advantages, Ge/ZnSe/GaAs heterostructures represent a model system for the study of a number of fundamental aspects of surface and −A\textsuperscript{III}B\textsuperscript{V} interfaces. However, this interface is complex with respect to stoichiometric reactivity. ZnSe-GaAs heterovalent heterostructures were fabricated and characterized by structural and electrical properties in [2]. The authors successfully fabricated the structures with quantum wells and GaAs islands in the bulk ZnSe. Growth of GaAs/ZnSe heterostructures

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was studied and heterovalent quantum structures of ZnSe-GaAs were fabricated using this approach and characterized by optical methods in [2]. Characteristics of the series of simple heterojunctions were studied in [3], which possess the following bonds: (1) only As-Zn, (2) only Se-Ga, and (3) As-Zn and Se-Ga mixed bonds and more complex interphase configurations, as well as a number of variants of interface stoichiometry. They showed that the interface energy can be expressed as a simple sum of the energies of pairs with one bond, with the mean error of less than 3%.

X-ray analysis showed that successive annealing of the ZnSe relaxed layer grown on GaAs (001) through molecular-beam epitaxy leads to the migration of Ga to ZnSe with a significant accumulation of As atoms near ZnSe. In the boundary regions of heterostructure, Ga,Se compound is formed as a side product, while Zn atoms diffuse from the interface to the GaAs substrate [4]. The authors of [5] studied the possibility of the growth of substitutional solid solution of (GaAs)x-y(ZnSe)y with ordered massive of nanosized crystals on the GaAs (100) substrates. The chemical composition of the grown epitaxial films was determined using an X-ray microanalyzer along the epitaxial layer thickness. The size of nanocrystals was evaluated using atomic force microscopy.

The author of [6] investigated X-ray diffractograms

\[ \Delta x = \sum_{i=1}^{m} z_i \delta x_i - \sum_{i=1}^{m} z_i \delta x_i = 0 \]

\[ \Delta r = \sum_{i=1}^{m} r_i \delta r_i - \sum_{i=1}^{m} r_i \delta r_i \leq 0.1 \sum_{i=1}^{m} r_i \]  

Where, and are valencies; and are covalent radii of the atoms of solvent \( m \) and soluble \( j \) chemical element or the elements forming molecules, respectively; and \( i = 1, 2, 3, 4 \) is the number of interacting elements. Condition (1) considers the electroneutrality of the soluble chemical elements or compound in dissolving semiconductor material. It is performed when soluble elements are isovalent with respect to the dissolving semiconductor. Condition (2) considers similar geometrical parameters of solvent \( m \) and soluble \( j \) compounds, which excludes significant lattice distortions in solid solutions. The lower the \( \Delta r \), the lower the \( \varepsilon \); consequently, the higher the crystallographic perfection of substitutional solid solution and the higher the solubility of \( j \) in \( m \). When the difference of the sum of covalent radii of the atoms of molecules forming solution is higher than 10%, the formation of continuous substitutional solid solutions of these components is insignificant. The case \( i = 1 \) reflects the conditions of formation of continuous substitutional solid solutions of the atoms of chemical elements of solvent A, B, ..., with atoms C, D, ..., of soluble element or compound and determined by formula A_i C or (AB)_i D, as exemplified by Si_i Ge and InAs_i Sb, where \( 0 \leq x \leq 1 \). If \( i = 2, \) Eqs. (1) and (2) reflect the conditions of formation of continuous substitutional solid solutions of two neighbouring solvent atoms with two-atomic molecule of soluble semiconductor according to formula (AB)_i (CD) or (C)_i (AB), as exemplified by (GaAs)_i (ZnSe)_j, (Ge)_i (GaAs)_j, or (Ge)_i (ZnSe)_j. Let us consider the conditions of the formation of continuous substitutional solid solutions on the basis of two-atomic and \( A^B^B \) and \( A^B^e \) compounds. In these systems, conditions (1) and (2) are the following:

\[ \Delta z = (z_{III} + z_{V}) - (z_{IV} + z_{IV}) = 0 \]

\[ \Delta z = (z_{III} + z_{V}) - (z_{II} + z_{VI}) = 0 \]

\[ \Delta z = (z_{IV} + z_{IV}) - (z_{II} + z_{VI}) = 0 \]
\[ \Delta r = \left| (z_{III} + z_V) - (z_{IV} + z_{IV}) \right| \leq 0.1, \left| (z_{III} + z_V) \right| \leq 0.1 \]

where \( z_{II} \), \( z_{III} \), \( z_{IV} \), and \( z_V \) are valencies and \( r_{II} \), \( r_{III} \), \( r_{IV} \), and \( r_V \) are covalent radii of the elements of groups II, III, IV, V, and VI, respectively.

Difference of the sum of covalent radii of the atoms of GaAs molecules and Ge \( \Delta r = 0\% \), while the difference of the sum of covalent radii of the atoms of GaAs and ZnSe molecules \( \Delta r = 0.4\% \). Difference of the lattice parameters of GaAs binary compounds and Ge \( \Delta a < 0.2\% \), while in the case of GaAs and ZnSe \( \Delta a < 0.3\% \). Mutual molecular substitution of these components does not significantly distort the crystal lattice and the energy of elastic distortions of lattice would be minimum; consequently, they form substitutional solid solution in the form of \((\text{GaAs})_{1-x}(\text{Ge})_x(\text{ZnSe})_x\) whose tetrahedral bonds are given in Fig. 1. shows the layer rich in gallium arsenide, where some GaAs molecules are replaced by pair atoms of Ge and ZnSe molecular compounds. Similar lattice parameters and smooth transition from gallium arsenide substrate to epitaxial layer of \((\text{GaAs})_{1-x}(\text{Ge})_x(\text{ZnSe})_x\) avoids mechanical stress arising in the substrate-film transient region.

Solid solutions of \((\text{GaAs})_{1-x}(\text{Ge})_x(\text{ZnSe})_x\) were grown on single-crystal GaAs substrates possessing (100) orientation with \( n \)-type conductivity \( n = 5 \times 10^{18} \text{ cm}^{-3} \) through the liquid-phase epitaxy. The substrates possessed a diameter of 20 mm and a thickness of \( \sim 350 \mu \text{m} \). A vertical quartz reactor with horizontal substrates was used to grow solid solution. 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 (Fig.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.

**Fig. 1. Spatial configuration of tetrahedral bonds of molecules of continuous solid solutions \((\text{GaAs})_{1-x}(\text{Ge})_x(\text{ZnSe})_x\).**

- As, – Ga, – Ge, – Zn, – Se
Fig. 2. Diagram of a graphite cassette with horizontally placed substrates and a solution-melt (the thickness of the gap between the substrates is $\delta = 1$ mm).

Therefore, we assume that GaAs, Ge$_2$, and ZnSe in Sn solution-melt are mainly in the form of Ga-As, Ge-Ge, and Zn-Se molecules (Fig. 2). Since the sum of the covalent radii of the atoms of the GaAs ($r_{Ga} + r_{As} = 2.43\, \text{Å}$), Ge$_2$ ($r_{Ge} + r_{Ge} = 2.41\, \text{Å}$) and ZnSe ($r_{Zn} + r_{Se} = 2.45\, \text{Å}$) is close and the sum of the valencies of their atoms is equal ($z_{Ga} + z_{As} = z_{Ge} + z_{Ge}$, $z_{Zn} + z_{As} = z_{Zn} + z_{Se}$), then the substitution of diatomic molecules at the crystal lattice sites of the solid solution is energetically more favourable than the atomic substitution of the crystal lattice site by Ga, As, Ge, Zn, or Se atoms separately.

For the preparation of a solution-melt, the solubility of GaAs, Ge$_2$, and ZnSe in Sn, in the temperature range 730–640°C, was studied by the method of weight loss of samples of gallium arsenide, germanium, and zinc selenium, placed in liquid tin and held in it until the solution saturation. The composition of the Sn-GaAs-Ge-ZnSe solution-melt at 730°C was as follows: Sn: 75 g, GaAs: 1.5 g, Ge: 1.5 g, and ZnSe: 1 g. We assume that the dissolved compounds GaAs, Ge$_2$, and ZnSe in liquid tin at a temperature of liquid-phase epitaxy (730°C) are mainly in the form of molecules GaAs, ZnSe and atom Ge. This assumption is based on the analysis of the solubility of GaAs, Ge$_2$, and ZnSe in Sn. The decomposition of Ge atoms and ZnSe molecules, when dissolved in Sn, into individual Ge, Zn, and Se atoms, according to the state diagram of the alloys, is equivalent to the simultaneous dissolution of Ge, Zn and Se in Sn. As is known, all these three substances Ge, Zn, and Se, and Sn at a temperature of 730°C are in a molten state (as their melting points are below 730°C) and have unlimited solubility among themselves. Figures 3 – a, b, c show data on the solubility of GaAs, Ge$_2$, and ZnSe in Sn as a function of temperature. Data for GaAs and Ge$_2$ are taken from the work of the authors [9] and for ZnSe, from the work of Kumar [10].
In Fig. 3. shows that, the solubility of GaAs, Ge\textsubscript{2} and ZnSe in Sn are clearly limited, and they are only 4.95 mole % (for GaAs), 1.05 at % (for Ge) and 0.41 mole % (for ZnSe) at 730°C respectively, which indicates that the dissolved GaAs, Ge\textsubscript{2}, ZnSe in the tin solution-melt is mainly in the form of Ga-As, Ge-Ge Zn-Se molecules. In addition, one of the main conditions of liquid-phase epitaxy is that the solution-melt must be supersaturated. The fact that under these conditions the epitaxial growth of (GaAs)\textsubscript{1-x} (Ge\textsubscript{2})\textsubscript{x} (ZnSe)\textsubscript{y} alloy because the solution-melt becomes supersaturated with the elements Ge and ZnSe at these temperatures. 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 (ϑ) were varied.

The surface condition of the grown epitaxial layers was investigated by atomic-force microscope. On the fig.4.a and b, two- and three-dimensional images of the surface of epitaxial films (GaAs\textsubscript{0.69}(Ge\textsubscript{2})\textsubscript{0.17}ZnSe\textsubscript{0.14}) are presented. In fact, that the crystallization of gallium arsenide layers occurs since at a chosen epitaxy temperature the solution is saturated by GaAs. At lower temperatures, conditions are implemented for the growth of (GaAs)\textsubscript{1-x} (Ge\textsubscript{2})\textsubscript{x} (ZnSe)\textsubscript{y} alloy because the solution-melt becomes supersaturated with the elements Ge and ZnSe at these temperatures. 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 (ϑ) were varied.

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formation of islet (nanostructures) is composed from the components (ZnSe) on the surface of the epitaxial layer in the growth process, that is stay the quantum dots almost the same size and different heights are formed (Fig. 4.b.). These quantum dots are created in the local electrostatic field at the distance 100–150 nm, that the intensity is $E = 10^7$–$10^9$ V/cm. According to Franz-Keldysh effect, such the strong local electric field should lead to the change in the band gap of the solid solution around the quantum dots.

The structural studies of the grown films, as with the substrates so the films were performed at 300 K on an improved X-ray diffractometer DRON-3M (CuKα - radiation, $\lambda = 0.15418$ nm) according to the scheme $\theta$ - 2$\theta$ in the mode of step scanning. The chemical composition of the epitaxial layers has been determined from the data of X-ray-structural analysis. There are several selective structural reflexes with different intensity in the X-ray pictures of epitaxial layers of $(\text{GaAs})_{1-x} (\text{Ge})_x (\text{ZnSe})_y$ (Fig. 5.). The analysis showed that the grown film has the sphalerite structure (ZnS) and it is the single crystal with orientation (100). The size nanocrystals films that estimated to the width of the main peak (400) is about 52 nm.

The lattice parameter of the film that defined according to the three reflections - (200), (400) and (600) by means of Nelson Reilly extrapolation function $\xi = (1/2) \cdot ([\text{Cos}$\theta$/\theta] + [\text{Cos}$\theta$/\text{Sin}$\theta])$ and it is $a = 5.6568$ Å. The structural maximum (440) with $d/n = 0.1001$ nm belongs to the crystal lattice of Ge nanocrystals with size ~ 44 nm. The value of the lattice parameter of the nanocrystals Ge that determined from X-ray picture amounted $a_{\text{Ge}} = 5.6625$ Å. The experimentally determined value of the parameter lattice of zinc selenium and arsenide gallium amounted $a_{\text{ZnSe}} = 5.6697$ Å and $a_{\text{GaAs}} = 5.6697$ Å, respectively. The size of the nanocrystals impurity phase of ZnSe estimated according to the width of the peak (600) is about 59 nm. It is shown that by the thickness of the film and the content of molecules Ge$_x$ and ZnSe varies within

The size of zinc selenium and arsenide gallium amounted $a_{\text{ZnSe}} = 5.6697$ Å, respectively. The X-ray film with the quantum dots of the ZnSe is shown in the Fig. 4.b. The size of the nanocrystals impurity phase of ZnSe estimated according to the width of the peak (600) is about 59 nm. It is shown that by the thickness of the film and the content of molecules Ge$x$ and ZnSe varies within

![Fig. 4. (a) two- and (b) three-dimensional images of the surface of epitaxial films (GaAs)$_{1-x} (Ge)_x (ZnSe)_y$ obtained by the atomic-force microscope. Image size is 700x700 nm, width and height of quantum dots are 12.6 and 128 ± 164 nm.](image1)

![Fig. 2. The X-ray picture of the epitaxial film of (GaAs)$_{1-x} (Ge)_x (ZnSe)_y$.](image2)
the range 0 ≤ x ≤ 0.17 and 0 ≤ y ≤ 0.14, which reduces the elastic stresses due to the mismatch parameters of lattice between the substrate and the film.

Thus, on the basis of the performed investigation results, analysis of (GaAs),ₓ(Ge)₁₋ₓ(ZnSe) solid solutions, it is possible to make the following conclusions:

1. Single-crystal (GaAs),ₓ(Ge)₁₋ₓ(ZnSe) solid solutions were grown on single-crystal n-GaAs substrates with (100) orientation from tin melt solution through liquid-phase epitaxy.
2. (GaAs),ₓ(Ge)₁₋ₓ(ZnSe) epitaxial layers were obtained at the distance between the upper and lower substrates δ = 1 mm, the temperature of the beginning of crystallization T = 730°C, the crystallization termination temperature T = 640°C, and the cooling rate υ = 1°C/min;
3. The grown epitaxial films of (GaAs),ₓ(Ge)₁₋ₓ(ZnSe) possessed thickness values of 10 μm and p-type conductivity with resistivities of 0.1 Ω cm and the concentration of carriers of 5.1·10¹⁷ cm⁻³, and the Hall mobility is μ = 359 cm²/(V·s) at room temperature.
4. Epitaxial films of (GaAs),ₓ(Ge)₁₋ₓ(ZnSe) have the sphalerite structure, molecules of ZnSe and Ge partially replaced molecules of GaAs in the defect-capable areas matrix on the borders and border areas of the section, followed by segregation of germanium ions and zinc selenium molecules to form nanocrystals (quantum dots) in these places.

References:
