Growing the solid solution of molecular substitution (GaAs)$_{1-z}$(ZnSe)$_z$

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Abstract: Epitaxial layers of semiconductor solid solutions of molecular substitution (GaAs)$_{1-z}$(ZnSe)$_z$ (0 < $z$ < 0.80) with a smoothly (but not monotonously) varying composition were obtained from the liquid phase on monocrystal GaAs (100) substrates. The solubility of gallium arsenide and zinc selenide in tin and the phase diagrams of binary systems Ga-Sn, As-Sn, Zn-Sn and Sn-Se indicate that binary compounds in the tin solvent at temperatures of 650–750°C, below the melting point of the corresponding materials, are not in the form of individual atoms of gallium, arsenic, zinc and selenium, but in the form of molecules of gallium arsenide and zinc selenide. Moreover, in the temperature range 650–750°C, the solubility of GaAs in tin varies from ~ 2.6 to ~ 5.5 mol%, and ZnSe - from ~ 0.2 to ~ 0.35 mol%, the solubility of gallium and zinc is unlimited, and the solubility of arsenic is more than 70 at.%, selenium - more than 5 at.%.

It is shown that due to the difference in the valence of gallium and arsenic atoms, the forces of chemical bonds between neighboring Ga and As atoms located in the tetrahedral lattice are not the same. In the tetrahedral lattice, each Ga atom forms 4 bonds with four neighboring As atoms, three of which are formed by the sharing of electrons of neighboring Ga and As atoms, and the fourth one only due to the two valence electrons of the As atom. Apparently, the ionic fraction of the fourth chemical bond is stronger than the other three.

1. Introduction
The development of modern semiconductor instrumentation is uninterruptedly linked with the success in improving the technology for producing traditional semiconductor materials, the development and research of new promising semiconductors. The great possibilities of semiconductor microelectronics are realized only with the development of the production of multifunctional semiconductor materials with various physical properties. In this aspect, semiconductor solid solutions of binary compounds III-V and II-VI have great opportunities [1-7]. The crystalline perfection of solid solutions is mainly determined by the crystal structures of the solution-forming components, as well as the geometric dimensions and charge states of the molecules of these components. Binary compounds GaAs and ZnSe have the same crystal structure (like zinc blende), and the lattice constants are $a_{\text{GaAs}} = 5.6532$ Å and $a_{\text{ZnSe}}$...
= 5.6676 Å, respectively. The sums of the valence of gallium (z_{Ga}) and arsenic (z_{As}) atoms, as well as zinc (z_{Zn}) and selenium (z_{Se}), are equal: z_{Ga} + z_{As} = z_{Zn} + z_{Se} = 8. Therefore, the binary compounds GaAs and ZnSe are suitable pairs for growing the semiconductor solid solutions of molecular substitution such as high quality (GaAs)\textsubscript{1-x}(ZnSe)\textsubscript{x}.

2. Objects and research methods
This paper is devoted to the technological features of liquid-phase epitaxy of the monocrystal solid solution of molecular substitution (GaAs)\textsubscript{1-x}(ZnSe)\textsubscript{x}.

The technological process of growing the semiconductor solid solution of molecular substitution (GaAs)\textsubscript{1-x}(ZnSe)\textsubscript{x} is given in [8]. Monocrystals GaAs(100) with a thickness of ~ 400 μm were used as substrates. For the growth of the epitaxial layer, the solution-melt (Sn-GaAs-ZnSe) was poured into the space bounded between two horizontally located substrates (Fig. 1). The substrates were fastened inside a graphite cassette. On the sides of the cassette there were slots for pouring the solution-melt. The technological growth process was carried out in the atmosphere of purified hydrogen.

![Figure 1. Schematic of the cassette with the Sn-GaAs-ZnSe solution-melt (the distance between the substrates is d = 1 mm).](image)

The solution-melt consisted of Sn-GaAs-ZnSe components. The process of growth of the epitaxial layer was carried out at 650-750°C, that is, at temperatures higher than the melting point of tin (231°C), but less than the melting temperature of gallium arsenide (1238°C) and zinc selenide (1525°C). At these temperatures, tin is in a liquid state. For the crystallization of the (GaAs)\textsubscript{1-x}(ZnSe)\textsubscript{x} solid solution, it is necessary that at these temperatures the tin solution be saturated with both gallium arsenide and zinc selenide. To ensure this condition, the solubilities of GaAs and ZnSe in Sn were studied. The state diagrams of binary systems Ga-Sn, As-Sn, Zn-Sn and Sn-Se were also studied.

3. Results and its discussion
The temperature dependence of the solubility of GaAs in tin is shown in Fig. 2a. We used the results of Vikram Kumar’s work on the solubility of ZnSe in tin [9] at different temperatures (Fig. 2 b).
Figure 2. Temperature dependence of the solubility of gallium arsenide (a) and zinc selenide (b) in tin.

In fig. 3 the diagrams of states of binary systems Ga-Sn (a), As-Sn (b), Zn-Sn (c) and Sn-Se (d) are presented. These results were taken from the work of M. Hansen and K. Anderko [10]. Analysis of the solubility of gallium arsenide and zinc selenide in tin at temperatures of 750 – 650°C (Fig. 2) as well as the phase diagrams of binary systems Ga-Sn, As-Sn, Zn-Sn and Sn-Se (Fig. 3) shows that these compounds at selected temperatures in tin are not in the form of individual Ga, As, Zn, and Se atoms, but in the form of GaAs and ZnSe molecules. If, upon dissolution of GaAs in tin, the substance decomposes into gallium and arsenic atoms, then this would be equivalent to the simultaneous dissolution of Ga and As in tin (Fig. 4 b).

As can be seen from Fig. 3 a, at temperatures above 231°C Ga and Sn are in a molten state, at temperatures 750–650°C the solubility of Ga in Sn is unlimited. At temperatures of 750–650°C, the solubility of As in Sn varies from 85 to 70 at.% (See Fig. 3 b). Consequently, if GaAs molecules decompose into separate Ga and As atoms upon dissolution of GaAs in Sn, then the solubility of GaAs in Sn should be at least 70 mol.% At 750–650°C. However, the solubility of gallium arsenide in tin at temperatures from 650 to 750°C varies from ~ 2.6 to ~ 5.5 mol.% (Fig. 2, a). Consequently, gallium arsenide in tin does not decompose into individual Ga and As atoms, but are in the form of GaAs molecules. This is clearly seen in Fig. 4.
Similarly from Fig. 3 it can be seen that at temperatures above 420°C Zn and Sn are in a molten state, the solubility of Zn in Sn at 650-750°C is unlimited. It can be seen from the Sn-Se phase diagram that when Se dissolves in Sn, the Se solubility at 650-750°C varies within the range from ~ 5 to ~ 12 at.% (Fig. 3d, tin angle of the phase diagram). Whereas, the solubility of ZnSe in Sn at 650-750°C varies from ~ 0.2 to 0.35 mol.% (See Fig. 2). Consequently, as in the case of gallium arsenide, zinc selenide in tin at 650–750°C does not decompose into individual Zn and Se atoms, but is in the form of ZnSe molecules, as shown in Fig. 5.

**Figure 3.** State diagrams of the binary system Ga-Sn (a), As-Sn (b), Zn-Sn (c) and Sn-Se (d).

**Figure 4.** Dissolution of the binary compound gallium arsenide in the form of molecules (a), as well as gallium and arsenic in the form of individual atoms (b) in tin at the temperature of 750°C.
Figure 5. Dissolution of the binary compound zinc selenide in the form of molecules (a), as well as zinc and selenium in the form of individual atoms (b) in tin at the temperature of 750°C.

One of the necessary conditions for the crystallization of a solid solution from the liquid phase is the need to saturate the tin solution-melt at a selected temperature with the components of the solid solution, that is, gallium arsenide and zinc selenide. The \((\text{GaAs})_{1-z}(\text{ZnSe})_z\) solid solution from the tin solution-melt (Sn-GaAs-ZnSe) at the component content of 4.6 mol.% GaAs and 0.3 mol.% ZnSe at the crystallization initiation temperature of 720°C was grown. But if binary compounds GaAs and ZnSe decompose into individual Ga, As, Zn and Se atoms, then according to the phase diagram of binary alloys (Fig. 3) at the specified content of components at 720°C the solution-melt will not be saturated not with gallium, not arsenic, not zinc and not selenium. Then the crystallization of the \((\text{GaAs})_{1-z}(\text{ZnSe})_z\) epitaxial layer should not have occurred. Crystallization of the solid solution \((\text{GaAs})_{1-z}(\text{ZnSe})_z\) under the chosen conditions indicates that the solution-melt is saturated with the molecules of the components, and there is no decomposition of the GaAs and ZnSe molecules into individual Ga, As, Zn, and Se atoms.

In fig. 6 shows the tetrahedral lattice of the GaAs binary compound. Atom Ga* (cational lattice site) and As* (anionic lattice site) are in the center of the corresponding tetrahedra. The Ga* atom has 3 valence electrons, and all of them will participate in the formation of covalent bonds with three neighboring As atoms - bonds (1), (2) and (3) (see Fig. 6). The As* atom has 5 valence electrons, 3 of which are involved in the formation of covalent bonds with three neighboring Ga atoms - bonds (5), (6) and (7) (see Fig. 6). The remaining two valence electrons participate in the formation of the bond with the Ga* atom - bond (4) (see Fig. 6). Since bonds (1), (2), (3), (5), (6) and (7) are formed by the sharing of electrons of neighboring Ga and As atoms, and bond (4) is only due to two electrons of the As* atom, then, apparently, the ionic fraction of the chemical bond (4) is stronger than the others. Consequently, relationship (4) is stronger than the others.
Figure 6. GaAs tetrahedral lattice. The dark circles represent electrons forming covalent bonds 1–7.

When GaAs is dissolved in the tin solvent at 650-750°C, the energy of thermal vibrations and the forces of interaction of Sn and GaAs atoms is sufficient to break covalent bonds (1), (2), (3), (5), (6) and (7), however, not enough to break the connection (4). Due to this, dissolved GaAs molecules will exist in the solution-melt, and not separate Ga and As atoms. A similar situation occurs when ZnSe dissolves in Sn at 650-750°C. Apparently, in binary compounds, there are asymmetries of the forces of interaction between the atoms of cations and anions.

The solid solution \((\text{GaAs})_{1-z}(\text{ZnSe})_z\) was grown on monocrystal GaAs substrates. The solution-melt was in close contact with the substrates. At the initial moment of crystallization, the solution-melt was supersaturated with gallium arsenide. Therefore, upon cooling, the epitaxial sublayer of gallium arsenide crystallizes. While cooling, a moment comes when the solution-melt is oversaturated with zinc selenide. From this moment on, the epitaxial layers of the \((\text{GaAs})_z(\text{ZnSe})_x\) solid solution with a variable composition crystallize. The optimization of the technological process of the growth of epitaxial layers was carried out by varying parameters such as the thickness of the solution-melt \((d)\), the growth temperature interval \((T)\), and the cooling rate of the solution-melt. Crystalline perfect layers were grown at \(d = 1\) mm, \(T = 720–650^0\) C, cooling rate of the solution-melt - 1 deg/min. In this case, the epitaxial layers had p-type conductivity and a thickness of 4 μm. The resistivity of the layers, determined by the Hall method, at 300 K was \(~ 180\) mΩcm, the Hall mobility was \(~ 60\) cm²/(Vs), the concentration of charge carriers was \(~ 310^{18}\) cm⁻³. The surface density of dislocation defects at the substrate-film interface was \(~ 10^7\) cm⁻², on the film surface \(~ 410^5\) cm⁻². The band gap of the near-surface layer of the solid solution \((\text{GaAs})_{1-z}(\text{ZnSe})_z\) \(z = 0.04\) is \(E_g = 1.45\) eV.

The chemical composition of epitaxial layers \((\text{GaAs})_{1-z}(\text{ZnSe})_z\) was determined using a Jeol JSM 5910 LV-Japan X-ray microanalyzer. Fig. 7 shows the profile of the distribution of As, Ga, Se, and Zn atoms over the thickness of the epitaxial layer. Analysis of the results of the fig. 7 shows that, upon crystallization of the epitaxial film, there is an intense substitution of gallium arsenide molecules by zinc selenide molecules at the sites of the crystal lattice of the solid solution. The maximum content of zinc selenide in the solid solution \(z = 0.80\) is achieved at an epitaxial layer thickness of 0.6 μm. Subsequently, as the film grows to the thickness of 1.7 μm, the content of zinc selenide molecules decreases rapidly, and then slowly to the thickness of 3.8 μm. On the surface layer, the molar content of zinc selenide is \(z = 0.04\).

The liquid phase epitaxy process takes place in an open system and in a limited volume. The system is two-phase - liquid (solution-melt) and solid (solid solution). During the process, heat is continuously...
removed from the system. The solution-melt is multicomponent. In such a system, a process of self-organization certainly arises. Crystallization of a solid solution with a variable composition is the result of the self-organization process of a multicomponent system. At 720°C, the solubility of zinc selenide in tin is an order of magnitude lower than the solubility of gallium arsenide. Therefore, after the intensive introduction of zinc selenide molecules into the solid phase, the solution-melt is depleted by these molecules, which causes a further decrease in the content of zinc selenide in the solid solution. The sublayer of the solid solution enriched with zinc selenide has a higher value of the band gap. Thus, the resulting epitaxial layer is a varyband gap semiconductor solid solution \((\text{GaAs})_{1-x}(\text{ZnSe})_x\) \((0 \leq x \leq 0.80)\) with a smoothly (but not monotonously) varying composition. A wider-gap sublayer of the \((\text{GaAs})_{0.8}(\text{ZnSe})_{0.2}\) solid solution is formed between the substrate and the near-surface epitaxial film.

![Figure 7. Distribution of As, Ga, Se, and Zn atoms over the depth of the \((\text{GaAs})_{1-x}(\text{ZnSe})_x\) epitaxial layer.](image)

4. Conclusion
Thus, the technological possibilities of obtaining the monocrystal semiconductor \((\text{GaAs})_{1-x}(\text{ZnSe})_x\) solid solution of molecular substitution are shown. Necessary condition for obtaining such a solid solution is the existence of the components of the solid solution in the liquid solution in the form of molecules, and not in the form of individual atoms, as well as the saturation of the solution-melt with molecules of the components of the solid solution.

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