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MORPHOLOGICAL STUDIES OF $(Ge_2)_{1-X}(ZnSe)_X$ SOLID SOLUTIONS

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Single-crystal films of the $(Ge_2)_{1-x}(ZnSe)_x$ solid solution from a limited tin solution-melt in the temperature range from 1023 K to 803 K at a cooling rate of 1-1.5 K/min on an EPOC installation were grown on Ge substrates and GaAs. The gap between the substrates was 0.65÷1.2 mm. It was established that the lowest values of dislocation density ($N_D=2\cdot10^4\div10^5$ cm^{-2}) were recorded in epitaxial films at T_{NC} = 893 K. Technological conditions for obtaining GaAs- $(Ge_2)_{1-x}(ZnSe)_x$ heterostructure with a smooth boundary have been achieved. Film substrate and the supercooling temperature was ΔT = 7.2°C.
Keywords: *Epitaxial layer; Heterostructure; Solid solution; Dislocation; Single-crystal*
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INTRODUCTION

The growth of crystalline perfect semiconductor solid solutions is of undoubted interest for the development of modern semiconductor instrumentation, since a solid solution synthesized from several semiconductor compound components, can combine the advantages of each of them [1,2]. Variable solid solutions belonging to the class $(C^{IV})_{1-x}(A^{II}B^{VI})_x$ make it possible to vary the basic electrophysical and photoelectric parameters of semiconductor materials within wide limits when their chemical compositions change [3,4]. We have obtained epitaxial layers $(Ge_2)_{1-x}(ZnSe)_x$, but to date, morphological studies that determine the photoelectric and electrophysical properties have not been sufficiently studied [5].

Defects and dislocations at the substrate-film interface serve as additional recombination centers, which worsens the injection properties in homo- and heterojunctions of the structure [6,7]. In addition, they significantly reduce the separation coefficient of light-generated electron-hole pairs in photoelectric converters [8]. Therefore, the selection of components and chemical compounds that form the necessary solid solutions is associated with many parameters that must be taken into account: sufficient solubility of the components in solvent at a given temperature; slight discrepancy between lattice parameters and thermal expansion coefficients of crystal-forming chemical compounds and substrates, crystal orientations, etc. [9,10].

It is known that solid solutions based on Ge ZnSe systems, depending on their chemical composition, allow the variation of basic electrophysical and optical parameters of semiconductor materials within a wide range. Considering the above, this work studied the conditions for forming solid solutions based on ZnSe and GeGe compounds and the features of their structure [11,12].

MATERIALS AND METHODS

The composition of the melt solution, consisting of Ge, ZnSe and Sn, was determined from the state diagrams of Sn–Ge–ZnSe alloys [11]. To prepare the liquid melt solution, we used the literature data described in [13,14].

Proven experimental scientific methods were used. Typically, substrates are used with certain smallest slopes during the growth of films from the liquid phase, which promote the formation of epitaxial layers on the surface of the substrate. Any surface of a solid has a certain roughness, so the surface energy is distributed unevenly and affects the growth of the solid solution on the substrate, as well as the formation of dislocations, which are associated with technological parameters, such as crystallization onset temperature (T_{OC}), growth rate (υ), gap between substrates (δ), composition of components in the melt solution with substrate orientations, etc.

The substrates were chemically pure (99.999%) Ge(111) and GaAs(100) plates with charge carrier concentration $n=(1\div5)\cdot10^{17}$cm^{-3}, $n=(4\div7)\cdot10^{17}$cm^{-3}, respectively, donor type of conductivity. The diameter and thickness of the substrate were 20 mm and 350-400 μm, respectively. To obtain a certain composition of the melt solution based on a tin solvent, germanium and zinc selenide powders were used.

To grow a graded-gap solid solution $(Ge_2)_{1-x}(ZnSe)_x$, we used a vertical-type quartz reactor with horizontally located substrates in an EPOS-type installation. The growth of the epitaxial layer was carried out from a small volume of tin solution-melt, limited to two substrates in the atmosphere, which were purified with palladium hydrogen, which

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made it possible to minimize the amount of consumed solution-melt. First, a vacuum was created in the reactor to a residual pressure of 10^{-2} Pa, then purified hydrogen was passed through the reactor for 30 minutes, and after that the heating process began. When the temperature reached the required value, the system switched to automatic mode. Homogenization of the melt solution was carried out within 40-50 minutes. Then the substrates on a graphite holder were brought into contact with the melt solution and, after filling the gaps between the substrates with the melt solution, they were raised 1 cm above the solution level. The growth of epitaxial layers $(Ge_2)_{1-x}(ZnSe)_x$ was stopped at the right moment by draining the melt solution from the substrates using a centrifuge.

The surface morphology of the grown films was studied using scanning electron microscopy (SEM EVO MA 10 (Zeiss)) and a CoreAFM setup.

Specific resistance, mobility and concentration of the main charge carriers were determined using an HMS-7000 installation (Hall effect measurement system).

EXPERIMENTAL AND DISCUSSION

Crystalline perfect epitaxial layers $(Ge_2)_{1-x}(ZnSe)_x$ were grown from a limited tin solution-melt with forced cooling (at a rate of 1-1.5 K/min) in the temperature range from 1023 K to 803 K on Ge(111) substrates, GaAs(100) [15]. A detailed description of the method used is presented in [16]. The resulting epitaxial layers were single-crystalline and had a sphalerite-type lattice, which is confirmed by XRD studies [15]. A detailed description of the method used is presented in [16]. The resulting epitaxial layers were single-crystalline and had a sphalerite-type lattice, which is confirmed by XRD studies [15]. Mutual substitution of components in the lattice did not lead to its noticeable deformation. That is, when replacing Zn and Se atoms located nearby in the lattice with germanium atoms, the energy of elastic distortions of the crystal lattice was minimal, therefore, the possibility of continuously forming a number of substitutional solid solutions, which can be designated as $(Ge_2)_{1-x}(ZnSe)_x$.

During the growth of an epitaxial film from a tin solution-melt, in the resulting varizone solid solution, the substitution process occurred by replacing atoms not separately statistically located in the lattice in Zn and Se with germanium atoms, and by replacing the Zn and Se atoms located in pairs in the lattice (the so-called dimers or “molecules" ZnSe in terminology [17]) for two germanium atoms (Ge-Ge), which contributed to the growth of epitaxial layers on the substrate. This process is schematically presented in Figure 1.

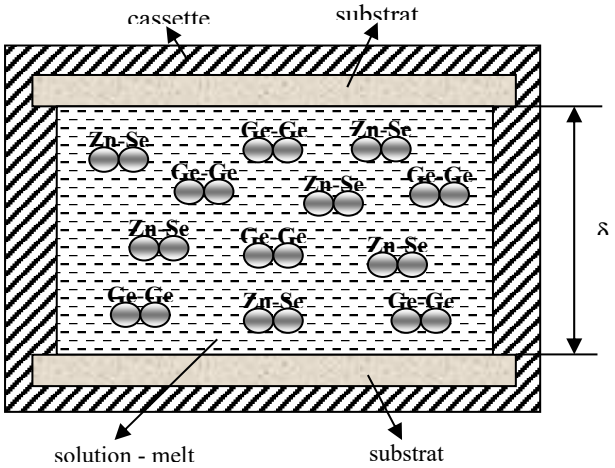


Figure 1. Scheme for the formation of a varizone solid solution from a Sn-Ge-ZnSe solution-melt (the thickness of the gap between the substrates δ = 1 mm).

In Figure -1 it is schematically shown the dissolved components Zn, Se, Ge in a tin solvent located between horizontally located substrates.

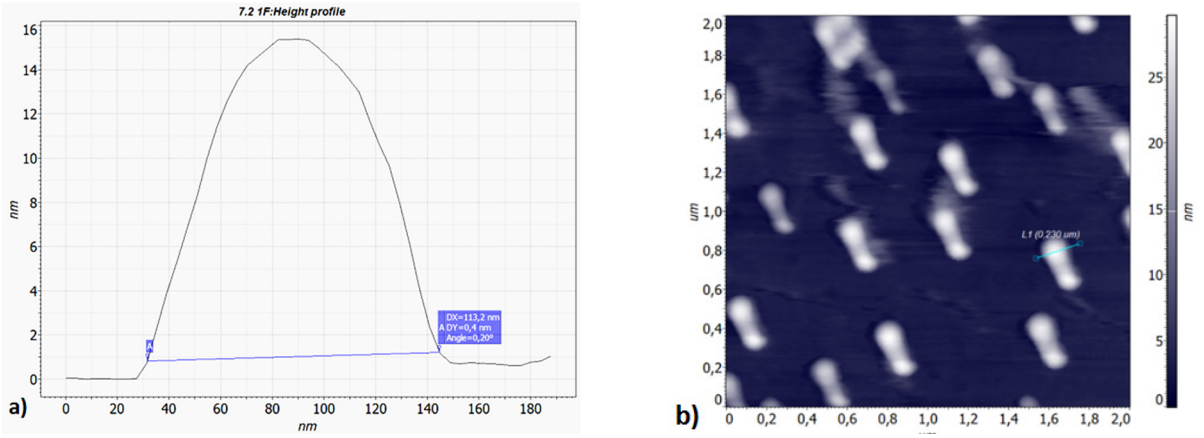
Epitaxial films $(Ge_2)_{1-x}(ZnSe)_x$ are grown from a Ge + ZnSe + Sn melt solution onto a Ge substrate without technological difficulties due to the saturation of the liquid phase relative to Ge + ZnSe; this prevents melting of the surface layer of the substrate-film interface at the front crystallization. If growth is carried out on a “foreign” GaAs substrate, then due to the unsaturation of the Ge + ZnSe + Sn system of the solution-melt relative to GaAs, it will lead to dissolution of the substrate. To prevent such a process, an equilibrium state of the system must be established between the liquid (solution-melt) and solid phase (substrate). Therefore, the liquid phase must be supercooled relative to the solid phase-substrate. For the thermodynamic equilibrium of this system, using the following formulas, you can determine the temperature or contact supercooling:

$$\Delta T = \frac{T_L}{\Delta H} \cdot \frac{EM}{1-\nu} \left(\frac{a_1 - a_2}{a_1}\right)^2 \cdot \frac{1}{f}.$$

Where, ΔH - the enthalpy of layer dissolution, T_L- the liquidus temperature, E and ν - Young’s modulus and Poisson’s ratio, M - the molar volume, a_1, a_2 - the lattice parameters of the substrate and the solid phase, f - the stabilization factor.

Based on theoretical calculations, the supercooling temperature for the solution-melt system Ge + ZnSe + Sn was predetermined and applied in the growth process. It has been established that when growing a $(Ge_2)_{1-x}(ZnSe)_x$ solid solution on a GaAs substrate from the liquid phase, the optimal supercooling temperature is $\Delta T = 7.2°C$. Thus, the technological condition for obtaining a GaAs- $(Ge_2)_{1-x}(ZnSe)_x$ heterostructure with crystalline perfection and a smooth substrate-film boundary has been achieved.

The resulting solid solution films were mirror-smooth, and to study their surface we carried out morphological studies. Three-dimensional images of the surface of the $(Ge_2)_{1-x}(ZnSe)_x$ epitaxial film obtained using an atomic force microscope showed that a quantum dot is formed in the surface layer with a width of 110 nm and a height of 14 nm (Figure 2 (a, b)).



a b

Figure 2. Three-dimensional **(a)** - (image size 2×2 μm^2) and two-dimensional **(b)** - image of the surface of epitaxial films $(Ge_2)_{1-x}(ZnSe)_x$, (quantum dot size: width 110 nm, height 14 nm)

The forming quantum dots in the form of a dipole are directed strictly in one direction, with the same slope, which indicates the monocrystalline nature of the resulting epitaxial film. The forming quantum dots in the form of a dipole are directed strictly in one direction, with the same bias, which indicates the orderliness of the grown layers and the monocrystalline nature of the resulting epitaxial film. The figure also shows that the film layers formed consist of pairs of ordered nanoclusters. This is probably due to the potential field of the surface layer.

And also, to study the morphology of the films, we selected the composition of the etchant (we used mixtures of concentrated hydrofluoric (HF), nitric (HNO_3) and acetic (CH_3COOH) acids, in the ratios $1hHF+3hHNO_3+4hCH_3COOH$). To identify dislocation, etch pits on the (111) plane, the samples were etched in a solution, then the etchant was diluted with deionized water and washed. After this process, using a scanning electron microscope (SEM), images of dislocations on the surface of the grown $(Ge_2)_{1-x}(ZnSe)_x$ epitaxial layers were obtained and the dislocation densities were determined. According to experimental data, the dislocation density N_D in grown semiconductor solid solutions $(Ge_2)_{1-x}(ZnSe)_x$ depended on many technological parameters: growth temperature, forced thorough cooling, orientation and cleanliness of substrates, type of solvent. Therefore, in order to reduce the dislocation density, experiments were carried out at different T_{OC} values. It was found that the lowest values of dislocation density ($N_D=2\cdot10^4\div10^5 cm^{-2}$) were recorded in epitaxial films at T_{OC} = 893 K (Figure 3).

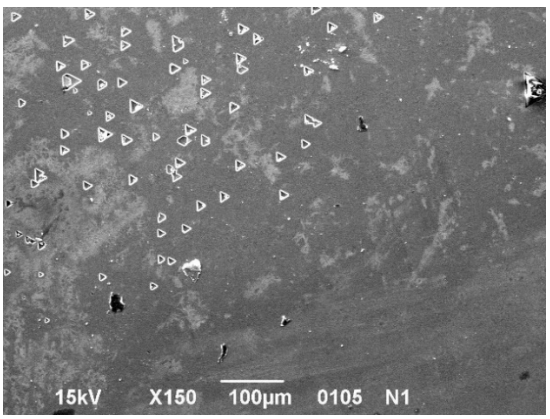


Figure 3. Photographs of dislocations on the surface of $(Ge_2)_{1-x}(ZnSe)_x$ epitaxial layers (obtained using SEM EVO MA 10 (Zeiss))

Subsequently, some electrophysical properties of the resulting films were studied: the resistivity, Hall mobility and charge carrier concentration at a temperature of 300 K were determined: $\rho = 0.5\div5$ Ohm·cm, $\mu_p = 30\div60$ cm^2/V·s, $n_p = (5\div7)\cdot10^{18}$ cm^{-3}. The films had hole type conductivity.

CONCLUSIONS

Thus, the possibility of obtaining crystalline perfect epitaxial layers of solid growth from a limited tin solution-melt is shown. Thieves $(Ge_2)_{1-x}(ZnSe)_x$ on GaAs substrates with (100) orientation and Ge with (111) orientation. Based on theoretical calculations, the supercooling temperature for the solution-melt of the Ge + ZnSe + Sn system was predetermined, which is equal to ΔT = 7.2 °C. The technological conditions for obtaining a solution-melt of GaAs-$(Ge_2)_{1-x}(ZnSe)_x$ heterostructures from the Ge + ZnSe + Sn system without sub-dissolution of the "foreign" substrate using supercooling have been established experimentally. It was found that the lowest values of dislocation density N_D=$2\cdot10^4\div10^5$ cm^{-2}) were recorded in epitaxial films at T_{OC} = 893 K. In the future, these solid solutions can be used as graded-gap semiconductor materials with controlled electrophysical and photoelectric properties in field of semiconductor instrument making.

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МОРФОЛОГІЧНІ ДОСЛІДЖЕННЯ ТВЕРДИХ РОЗЧИНІВ $(Ge_2)_{1-X}(ZnSe)_X$

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Монокристалічні плівки твердого розчину $(Ge_2)_{1-x}(ZnSe)_x$ з обмеженого розчину-розплаву олова в діапазоні температур від 1023 К до 803 К при швидкості охолодження 1-1,5 К/хв на установці ЕРОС були вирощені на підкладках Ge та GaAs. Зазор між підкладками становив 0,65÷1,2 мм. Встановлено, що найменші значення густини дислокацій (ND=$2\cdot10^4\div10^5$ cm^{-2}) зафіксовано в епітаксіальних плівках при TNC = 893 К. Були досягнуті технологічні умови отримання гетероструктури GaAs-$(Ge_2)_{1-x}(ZnSe)_x$ з гладкою межею. Температура плівкової підкладка і переохолодження становила ΔT = 7,2°C.

Ключові слова: *епітаксіальний шар; гетероструктура; твердий розчин; дислокація; монокристал*