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Growth of $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ Epitaxial Films on Si Substrates by Liquid-Phase Epitaxy

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Abstract. It was determined that at gaps between substrates more than 0.8 mm, the process of mass supply, when growing epitaxial layers $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$, is also affected by convection flows arising under the action of gravitational force. It was determined that at the temperature of the beginning of epitaxy T = 750°C, a continuous layer $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ with nanoislands was grown on Si substrates. This causes the lattice mismatch by 4% and the difference in the linear thermal expansion coefficients of the substrate and the solid solution component, respectively. The grown film is a substitution solid solution $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ ($0 \le x \le 0.53$ and $0 \le y \le 0.74$) with a gradually changing composition.

Keywords: Substrate, epitaxial layer, convection flow, gravitational force, temperature, nanoislands, solid solution**.**

Аннотация. Определено, что при зазорах между подложками более 0,8 мм на процесс подачи массы при выращивании эпитаксиальных слоев $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ также влияют конвекционные потоки, возникающие под действием гравитации. Установлено, что при температуре начала эпитаксии T = 750°C на подложках Si выращивается сплошной слой $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ с наноостровками. Это приводит к несоответствию решеток на 4% и разнице в коэффициентах линейного теплового расширения подложки и компонента твердого раствора соответственно. Выращенная пленка представляет собой твердый раствор замещения $Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ ($0<x<0{,}53$ и $0<y<0{,}74$) с постепенно меняющимся составом.

Ключевые слова: Подложка, эпитаксиальный слой, конвекционное течение, сила гравитации, температура, нанооствровки, твердый раствор.

Аннотация. Тагликлар орасидаги бўшлиқлар 0,8 мм ортиқ бўлганида $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ эпитаксиал қатламларни ўстиришда масса таъминоти жараёнига тортишиш кучи остида пайдо бўладиган конвексия оқимлари ҳам таъсир қилаши аниқланди. Эпитакцияланишнинг дастлабки ҳарорати T = 750°C да Si тагликларида нанооролларга эга бўлган узлуксиз қатлам $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ шаклланиши аниқланди. Бу панжара қийматларини мос келмаслигини 4% га ва таглик ва қаттиқ қоришма компонентининг чизиқли термал кенгайиш коеффитсиентларидаги фарқни туфайли юзага келади. Ўстирилган $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ плёнка аста-секин ўзгарувчан таркибга эга бўлган ўрин алашинувчи қаттиқ қоришма ҳисобланади ($0 \le x \le 0{,}53$ ва $0 \le й \le 0{,}74$).

Калит сўзлар: Таглик, эпитаксиал қатлам, конвексия оқими, тортишиш кучи, ҳарорат, нанооролар, қаттиқ қоришма.

1. Introduction

It is known that many A^2B^6 and A^3B^5 compounds are expensive materials, and therefore the use of massive elements based on them on a large scale is economically unprofitable. Taking into account that the active area of optoelectronic elements is several micrometers, it is reasonable to grow such compounds on affordable and cheap substrates, made, in particular, from single-crystal silicon. However, due to the difference in the lattice parameters and thermal expansion coefficients of silicon and epitaxial films of A^2B^6 and A^3B^5 compounds grown on it, it is difficult to obtain high-quality films directly on silicon substrates. These inconsistencies can be eliminated by using an intermediate buffer layer embedded between the substrate and the epitaxial layer. Recent work aimed at careful control and design of heterostructure preparation Ge/Si with Ge quantum dots into delocalized states of the Si valence band [9]. 100 nm thick germanium buffer layers, then, a Ge quantum dot layer with an effective thickness was grown at the appropriate crystallization temperatures. Taking into account the mechanics of the epitaxial film and the properties of isovalent interfaces in the design of the epitaxial structure was used to create high-quality heterostructures Ge/Si capable of supporting further growth of GaAs and ZnSe layers for micro- and optoelectronic devices, since, Ge with GaAs and ZnSe compounds, which practically matches in lattice parameter (0.15% lattice mismatch at 300 K). In addition, the coefficient of thermal expansion of the GaAs and ZnSe compounds differ by 3% and 15%, respectively. In the

above studies, $(Ge_2)_{1-x}(GaAs)_x$ and $(Ge_2)_{1-x}(ZnSe)_x$ epitaxial layers on Si substrates were grown by metal chemical vapor deposition and molecular beam epitaxy. However, despite the emerging progress in integrating GaAs and ZnSe compounds with Si technology and the emergence of instrumental applications, heteroepitaxy of $(Ge_2)_{1-x}(GaAs)_x$ and $(Ge_2)_{1-x}(ZnSe)_x$ on Si substrates still remains a difficult problem.

In this regard, in this paper, experimental results are presented on the possibility of growing an epitaxial layer $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ on Si substrates through a Ge buffer layer.

2. Technique for Growing $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ Epitaxial Films on Si Substrates.

Solid solutions $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ were grown on GaAs substrates by liquid-phase epitaxy from a bismuth solution-melt. The substrates were oriented along the (111) directions. The crystallization onset temperature was 750°C. The composition of the solution-melt, corresponding to the temperature of the beginning of crystallization, was also determined from the phase diagram of Bi-Ge, Bi-GaAs and Bi-ZnSe and has the following ratio of components (in mass percent): Bi:97.63%, Ge:3.13%, GaAs:1.18 %, and ZnSe:0.48%. The formation of a solid solution of molecular substitution between Ge_2, GaAs, and ZnSe has been studied. According to the criteria, the following conditions must be met for the formation of a substitutional solid solution [10]: the sums of the valencies of the atoms of the molecules of the substituting components of the solid solution must be the same; the sums of the covalent radii of the atoms of the molecules of the substituting components should not differ by more than 10%. According to calculations, Ge_2, GaAs, and ZnSe can form a continuous substitutional solid solution with molecular substitution (Fig.1), but they cannot be done with atomic substitution.

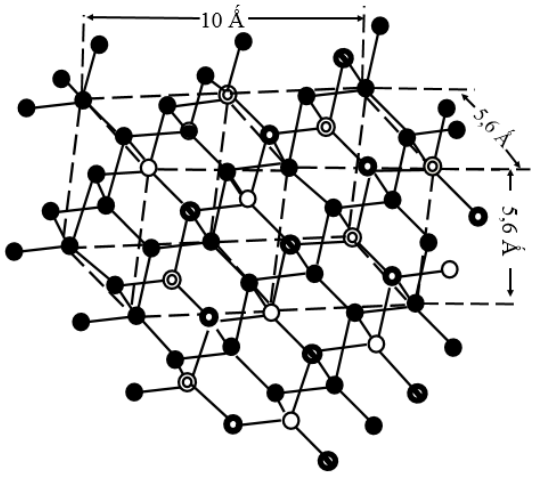

Fig. 1. Spatial configuration of letrahedral bonds of molecules of continuous solid solutions $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$

●- Ge, ◐- Ga, ◎- As, ○- Zn, ◔- Se

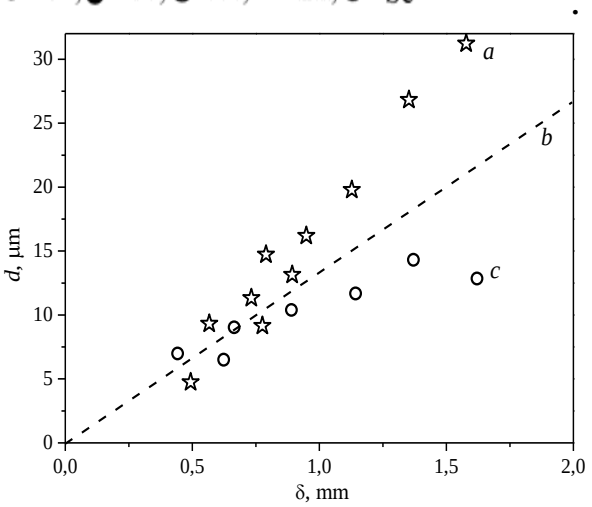

Fig. 2. Dependences of the bonds of thickness of epitaxial of solid solutions $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ on the gap between the substrates. *a* – for the upper substrate, *b* – theoretical dependence, *c* – the lower substrate.

The experimental data are given in Fig 2, within the thickness measurement errors, lie on line described by the expression

$$d_{(Ge)_{1-x-y}(GaAs)_x(ZnSe)_y} = \frac{\delta}{2}\left[\frac{A_1}{\rho_1}(1-x-y)+\frac{A_2}{\rho_2}x+\frac{A_3}{\rho_3}y\right]\cdot\frac{\rho}{A}[C_1+C_2+C_3] \quad (1)$$

Until a gap ~ 0.8 mm is reached, after which the experimental curves for both the lower and upper substrates strongly diverge from the theoretical ones. Where, x and y are the content of GaAs and ZnSe in the solid solution, A_1, A_2, A_3, A and p_1, p_2, p_3, p are the molecular weights and densities of germanium, gallium arsenide, zinc selenide and bismuth, respectively: C_1, C_2, C_3 molecular fractions germanium, gallium arsenide and zinc selenide in the liquid phase: δ size of the gap between the substrates. Since the molecular weights and densities of germanium and zinc selenide are very close in magnitude $\frac{A1}{p1} \approx \frac{A2}{p2} \approx \frac{A3}{p3}$, then the slopes of the theoretical straight lines described by expression (1) are almost the same for different "x" and "y". It should also be noted that the structural perfection of the layers of solid solutions grown on the lower and upper substrates also differ from each other. More perfect epitaxial layers with a smooth surface, other things being equal, are obtained on the lower substrates. We also note that with an increase in the temperature of the onset of epitaxy,

the structural perfection of the layers grown both on the lower and upper substrates improves.

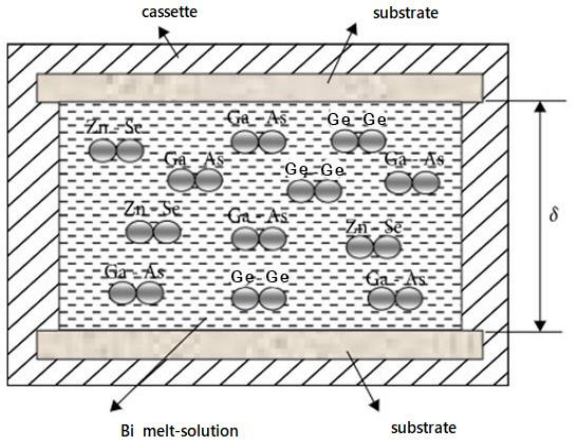

Fig. 3. Scheme of the distribution of components in the solution-melt located between the substrates at δ>0.8 mm during crystallization.

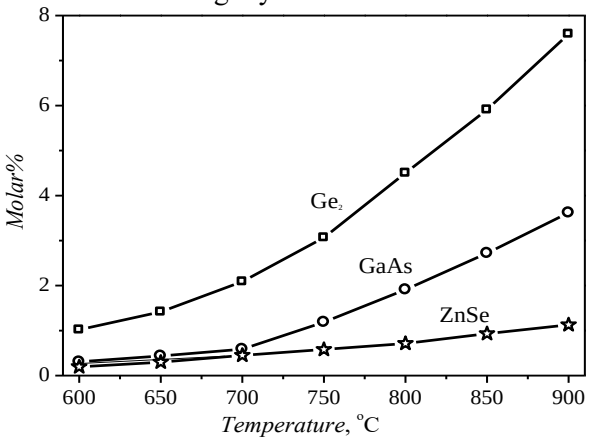

Fig. 4. Temperature dependence of Ge_2, GaAs, and ZnSe solubility in Bi.

The obtained dependences of the thickness of the epitaxial layers on the size of the gap "δ" at large gaps can be explained as follows (Fig3). In a melt solution kept at a certain temperature, the dissolved components are distributed uniformly throughout the entire volume of the melt solution, and since the melt solution was saturated both with respect to germanium and respect to zinc selenide, a solid solution $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ in the liquid phase, which begins redistributing in the solution-melt under the influence of the gravitational field. Thus, convection flows arise in the solution-melt. Since, the density of the solid solution $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ is less than that of the solvent, such convection flows enhance the supply of the mass of the solid solution to the upper crystallization front. Therefore, ceteris paribus, the actual growth rate of the layers on the top substrate is much higher, which probably contributes to the formation of thicker films. An increase in the growth rate also leads to a deterioration in the structural perfection of the layers. With gaps smaller than 0.8 mm, the conditions for the formation of convection flows in the solution-melt are probably insufficient and growth occurs only due to molecular diffusion of the components.

To prepare a melt solution, the solubility of Ge_2, GaAs, and ZnSe in Bi in the temperature range of 750÷650°C was studied by the mass loss method of Ge_2 , GaAs, and ZnSe samples placed in liquid bismuth and kept in it until the solution saturates. The composition of the Bi - Ge - GaAs-ZnSe melt solution at 730°C was as follows: Bi: 100 g, Ge: 3 g, Ge: 2 g and ZnSe: 1 g bismuth at the temperature of liquid phase epitaxy (750°C), which are mainly in the form of molecules. This assumption is based on the analysis of the solubility of Ge_2, GaAs and ZnSe in Bi . Decomposition of Ge_2, GaAs and ZnSe atoms upon dissolution in Bi into separate Ga, As atoms Zn and Se, according to the state diagram of the alloys, is equivalent to the simultaneous dissolution of Ga, As Zn and Se to Bi. As is known, all these quadrants of the substance Ga, As Zn and Se and Bi are in a molten state at 750°C (since their melting points are lower (750°C) and have unlimited mutual solubility.

Fig. 4 shows data on the solubility of Ge_2, GaAs and ZnSe in Bi as a function of temperature. From Fig. 4, it can be seen that the solubility of Ge_2, GaAs and ZnSe in Bi is clearly limited, and they are only 3.1 mole% (for Ge), 1.18 mole% (for GaAs) and 0.57 mole% (for ZnSe) at 750 °C, respectively, which indicates that the dissolved Ge_2, GaAs and ZnSe in the bismuth melt solution are mainly in the form of Ge-Ge molecules Ga-As , Zn-Se. In addition, one of the main conditions for liquid-phase epitaxy is that the solution-melt must be supersaturated. The fact that epitaxial growth of $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ is observed under these conditions indicates that the solution-melt of tin is saturated with Ga-As , Ge-Ge Zn-Se and that these molecules do not disintegrate into individual atoms. Based on the principle of similarity, that is, "like dissolves in like", it can be assumed that at the initial moment of growth of the epitaxial layer, germanium layers crystallize, since at the selected epitaxy temperature the solution is saturated with Ge. At lower temperatures, conditions are favorable for growing of the $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ alloy, since the melt solution becomes oversaturated with Ge and ZnSe at these temperatures. The samples were grown at different values of the liquid-phase epitaxy parameters. The distance between the upper and lower substrates (δ), as well as the beginning and end of the crystallization temperature (T) and

the rate of forced cooling of the tin melt solution (ϑ) varied.

3. Electron microscopic examination and X-ray microprobe analysis of solid solutions $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$.

The morphology of the layers was studied at the Solver-NEXT atomic force microscope. Fig.5 shows that at the temperature of the beginning of epitaxy T=750°C, a continuous layer with islands was grown on Si substrates. However, such layers had a matte surface and many nanoscale objects, i.e. nanoislands. This result should be expected, since the lattice mismatch (a_{Si} = 5.43 Å) ($a_{GaAs} \approx a_{Ge} \approx a_{ZnSe}$ = 5.65 Å) in this case is 4%. In addition, the linear coefficients of thermal expansion differ greatly from each other: at room temperature $\alpha_{Si} = 5.1 \cdot 10^{-6}$ deg^{-1}, $\alpha_{Ge} = 6.1 \cdot 10^{-6}$ deg^{-1}, $\alpha_{GaAs} = 5.9 \cdot 10^{-6}$ deg^{-1} and $\alpha_{ZnSe} = 7 \cdot 10^{-6}$ deg^{-1}. Such the lattice mismatch and difference in thermal expansion coefficients [11] probably led to forming nanoislands of the epitaxial layers of solid solutions $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$, which were observed in experiments.

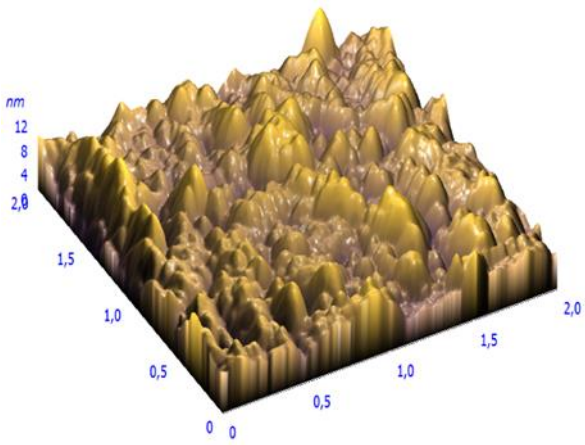

Fig 5. Atomic - force microscopic image of the surface of a solid solution $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ grown at T_c. = 750°C.

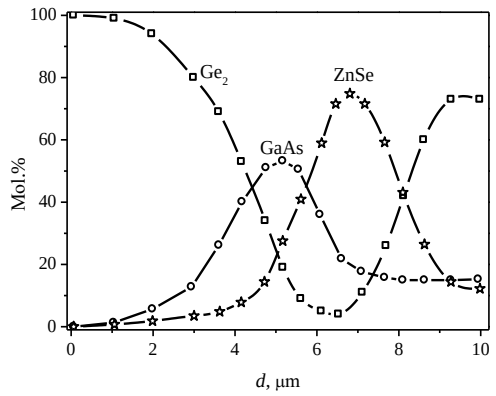

Fig 6. Distribution profile of Ge_2, GaAs and ZnSe molecules in the epitaxial layer $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$, d = 0 corresponds to the boundary between the substrate and the film

The study of the chemical composition of the grown epitaxial layers $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ was carried out on an X-ray microanalyzer " Jeol " JSM 5910 LV - Japan . Based on the results of X-ray microprobe analysis, the distribution profile of Ge_2 molecules was determined GaAs and ZnSe depending on the depth of the epitaxial layer. Fig.6 shows that with the growth of the solid solution $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$, the molar content of GaAs and ZnSe in the epitaxial layer first gradually increases, reaching the maximum value x = 0.53 and y = 0.74 respectively. This indicates a high supersaturation of the solution-melt at the crystallization front of GaAs and ZnSe. Further, the molar content of GaAs and ZnSe slowly decreases, reaching the values x = 0.15 and y = 0.12 in 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 GaAs is 3 times, and ZnSe 5 times lower than the solubility of Ge in bismuth, after the intensive introduction of GaAs and ZnSe into the solid phase, the solution-melt becomes depleted, which subsequently causes a gradual decrease in molar content of GaAs and ZnSe in the growth direction [12]. At a depth of 1 μm from the film surface, the molar content of GaAs and ZnSe does not exceed 15% and 12%, respectively.

Thus, the grown film is a substitution solid solution $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ ($0 \le x \le 0.53$ and $0 \le y \le 0.74$) with a gradually changing composition. A broadband layer enriched in GaAs and ZnSe is formed between the substrate and the surface region of the film.

Conclusion

Thus, based on the analysis of the technological modes of growing epitaxial films $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ on Si substrate and the results of morphological and X-ray microprobe analysis of studies, the following conclusions can be drawn: It was determined that at gaps between substrates more than 0.8 mm, the process of mass supply, when growing epitaxial layers $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$, is also affected by convection flows arising under the action of gravitational force. It was determined that at the temperature of the beginning of epitaxy T = 750°C, a continuous layer $(Ge_2)_{1-x-y}(GaAs)_x(ZnSe)_y$ with nanoislands was grown on Si substrates. This causes the lattice mismatch by 4% and the difference in the linear thermal expansion coefficients of the substrate and the solid solution component, respectively. The

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