Growth of Solid Solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ on Silicon Substrates by Liquid Phase Epitaxy

Akramjon Y. Boboev[1,*], Ulugbek. R. Karimberdiev[1], Sardor. R. Kadirov[2] and Nuritdin Y. Yunusaliyev[1]

[1] Faculty of Physics and Technology, Andijan State University, Andijan, 170100, Uzbekistan
[2] Faculty of Physics, Urgench State University, Urgench, 221100, Uzbekistan
*Corresponding Author: A. Y. Boboev. Email: aboboevscp@gmail.com

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ABSTRACT: This paper investigates the possibility of growing solid solutions of the composition $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ on silicon substrates using a germanium (Ge) buffer layer. The optimal conditions for obtaining a structurally high-quality epitaxial layer have been determined. In the study, the solid solution was obtained by liquid-phase epitaxy from a bismuth-containing melt solution. Epitaxial growth was carried out in a palladium-purified hydrogen atmosphere at a cooling rate of 1 ÷ 1.5°C/min in the temperature range 750 ÷ 650°C. Experimental data showed that the growth of the epitaxial film significantly depends on the size of the gap between the substrate and the starting material: the average symmetrical gap was 0.8 mm with a dispersion of 0.1 mm. Crystallisation occurred under the combined influence of diffusion and gravitational flow processes. Epitaxial films with a thickness of up to 10 μm demonstrated p-type conductivity with a specific resistance of about 10 Ω·cm and a carrier concentration of 1.5×10^{16} cm^{-3}. At a temperature of 750°C, the formation of nanoclusters was observed, which is associated with a 4% mismatch in lattice parameters and a difference in the thermal expansion coefficients of the components. The solid solution $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ (at $0 \le x \le 0.53$, $0 \le y \le 0.74$) was characterised by a gradient composition. At a depth of 1 μm, the GaAs and ZnSe content did not exceed 15% and 12%, respectively.

KEYWORDS: Solid solution; liquid phase epitaxy; Ge buffer layer; GaAs:Bi; ZnSe; diffusion; crystal defects

1 Introduction

In recent years, significant progress has been made in the field of silicon photonics, which aims to integrate optical data processing with silicon microelectronic technologies [1]. Such integration requires considerable effort and is gradually becoming increasingly important for the development of high-speed technological solutions of the next generation. The focus is on the monolithic growth of III-V binary compounds with a direct band gap on silicon (Si) substrates, which mitigates the problems associated with indirect band gaps in silicon [2]. It should be noted that this technological approach also plays a key role in reducing the reuse of expensive small substrates and ensures compatibility with traditional silicon technologies, including integrated photonic systems [3]. At the same time, improving the efficiency of low-frequency technologies and reducing the cost of solar cells with variable band gap width remain important tasks [4,5]. However, high-quality epitaxial growth of III-V and II-VI materials on silicon is associated with serious difficulties due to differences in crystal lattice parameters, thermal expansion coefficients, and material polarity. One approach to overcoming these difficulties is isovalent atomic doping of silicon, which increases its potential for integration into existing microelectronic processes. Nevertheless, certain problems remain, especially when growing germanium layers on silicon substrates. Fundamental differences in material properties, including lattice parameters, thermal expansion coefficients, and energy band configurations, contribute to the formation of electrically active crystal defects, such as stacking faults and dislocations [6–8]. Recent research has focused on the precise design of Ge/Si heterostructures, in particular on the study of germanium quantum dots, which have been found to influence delocalised electronic states in the valence band of silicon [9]. These developments are of great importance for micro- and nanoelectronic applications. In most experiments on Ge deposition on Si, a germanium buffer layer with a thickness of

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about 100 nm is created, followed by the formation of a layer of Ge quantum dots with an effective thickness of about 1 μm under optimal crystallisation conditions. Taking into account the mechanics of epitaxial films and the behaviour of isovalent interfaces when designing heterostructures has made it possible to obtain high-quality Ge/Si structures suitable for the subsequent deposition of GaAs and ZnSe layers for the purpose of creating microelectronic and optoelectronic devices. This approach is particularly promising because the combination of Ge with GaAs and ZnSe provides virtually identical lattice parameters (the discrepancy is only ~0.15% at 300 K). At the same time, the thermal expansion coefficients of GaAs and ZnSe differ by approximately 3% and 15%, respectively.

Previous studies [10–12] reported on the heteroepitaxial growth of $(Ge_2)_{1-x}(GaAs)_x$ and $(Ge_2)_{1-x}(ZnSe)_x$ compounds on silicon substrates using MOCVD and MBE methods. However, despite the progress achieved in the integration of GaAs and ZnSe into silicon systems and their practical application, the epitaxial growth of solid solutions $Ge_2)_{1-x}(GaAs)_x$ and $(Ge_2)_{1-x}(ZnSe)_x$ on Si substrates remains a technologically challenging task. Based on the above, this paper presents experimental data on the synthesis of solid solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ grown on silicon substrates.

2 Growth of Epitaxial Layers $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$

Solid solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ were grown on silicon substrates with high structural perfection using liquid phase epitaxy. The thermodynamic conditions of the process were carefully optimised to ensure the dissolution of Ge_2, GaAs and ZnSe in bismuth-containing solvents in the form of molecular complexes. This approach allows the formation of a molecularly substituted solid solution in which germanium atoms replace dumbbell-shaped structural fragments of GaAs and ZnSe in the composition of epitaxial films. The use of this method ensures the deposition of GaAs and ZnSe layers with a continuously changing composition, which contributes to a smooth transition from Ge_2 to GaAs and ZnSe. The crystallisation of the solid solution is carried out under conditions close to thermodynamic equilibrium. To achieve high-quality crystal growth, it is critical to precisely control the cooling rate of the melt solution, maintaining it at a low level. This allows for an increase in the residence time of GaAs, ZnSe, and germanium pair atoms at the phase boundary, promoting the formation of an ordered crystal lattice. The formation of dumbbell-type defects is most likely in areas of the crystal lattice with the greatest chemical bond instability, where the film components are most susceptible to local structural rearrangement. Nevertheless, the controlled formation of such defects under appropriate conditions promotes the growth of films with a high degree of crystalline order and improved physicochemical properties. This study focuses on analysing the conditions for forming a molecularly substituted solid solution involving Ge_2, GaAs, and ZnSe. To successfully obtain such a solid solution, a number of fundamental conditions must be met [13]: the substitution of atoms must not lead to a change in the number of valence electrons involved in the formation of chemical bonds; the total covalent radii of the substituting and substituted atoms must not differ by more than 10%. Based on the above calculations, it can be concluded that Ge_2, GaAs and ZnSe compounds are capable of forming a continuous molecularly substituted solid solution, as shown in Fig. 1. However, these materials do not demonstrate the ability to form a solid solution by simple atomic substitution.

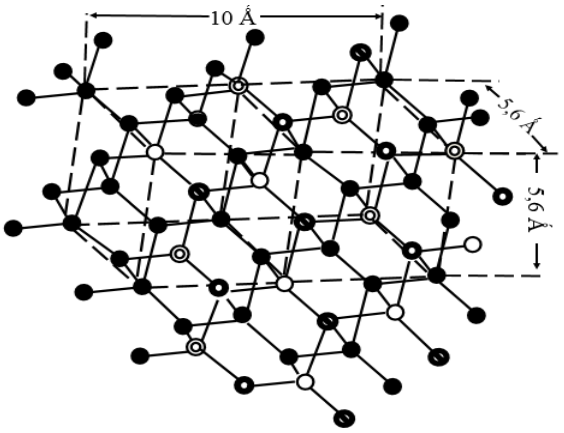

Figure 1: Spatial configuration of tetrahedral bonds in solid solution molecules.

Fig. 2 shows experimental data which, taking into account the thickness measurement error, are in good agreement with the linear dependence described by the following equation [14]:

$$d_s = \frac{a}{2}\left[\frac{A_1}{\rho_1}(1-x-y)+\frac{A_2}{\rho_2}x+\frac{A_3}{\rho_3}y\right]\cdot\frac{\rho}{A}[C_1+C_2+C_3] \quad (1)$$

where: x and y are the molar fractions of $GaAs_{1-\delta}Bi_\delta$ and ZnSe in the epitaxial film, A_1, A_2, A_3, A are the molecular masses of Ge, GaAs, ZnSe and Bi (solvent), ρ_1, ρ_2, ρ_3, ρ are the densities of Ge, GaAs, ZnSe and Bi, respectively, C_1, C_2, C_3, C are the molecular fractions of Ge, GaAs and ZnSe in the liquid phase; a is the gap between the substrates (approximately a ≈ 0.8 mm); d is the film thickness. Up to a gap value of a ≈ 0.8 mm, the experimental dependencies for the upper and lower substrates show good agreement with the calculated values according to the above equation. However, with a further increase in the gap, a significant deviation between the experimental and theoretical curves is observed.

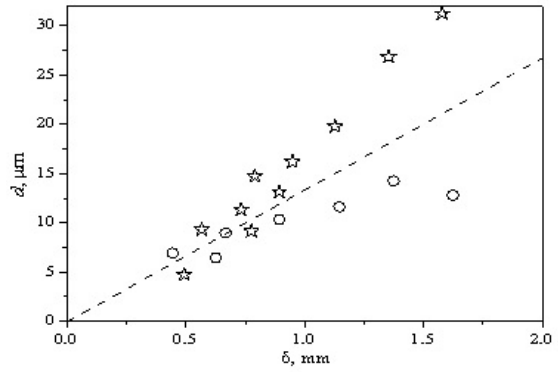

Figure 2: Dependence of the thickness of epitaxial layers of solid solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ on the gap between substrates.

It is noteworthy that the molecular masses and densities of Ge and ZnSe are close in value, which allows the approximation: $\frac{A_1}{\rho_1} \approx \frac{A_2}{\rho_2} \approx \frac{A_3}{\rho_3}$ to be applied. As a result, the slopes of the theoretical lines

obtained from Eq. (1) practically coincide at different values of "x" and "y", which further confirms the linear nature of the dependence of the layer thickness on the composition.

Particular attention should be paid to the quality of the structural layers formed on the upper and lower substrates. As a rule, epitaxial films deposited on lower substrates demonstrate a higher degree of crystalline order and surface smoothness under otherwise equal conditions. This effect is explained by differences in the thermal gradient and mechanical stresses arising during the growth process. In addition, increasing the initial epitaxy temperature has a positive effect on the structural integrity of the deposited layers on both the lower and upper substrates. The improvement in structure in this case is due to the intensification of atomic diffusion processes and the relaxation of internal stresses, which contributes to the formation of a more homogeneous and high-quality crystal structure. The observed dependence of the thickness of epitaxial layers on the value of the gap a (especially when it increases) can be explained as follows (see Fig. 3). In a melt-solution maintained at a given temperature, its components are distributed uniformly throughout the volume. Since the liquid phase is saturated with both germanium (Ge) and zinc selenide (ZnSe), a molecularly substituted solid solution of the composition $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ is formed in it. Under the action of the gravitational field inside the melt, the components are redistributed, causing the formation of convective currents. However, the intensity of such currents is determined not only by the difference in the densities of the components, but also by the peculiarities of heat and mass transfer in the system.

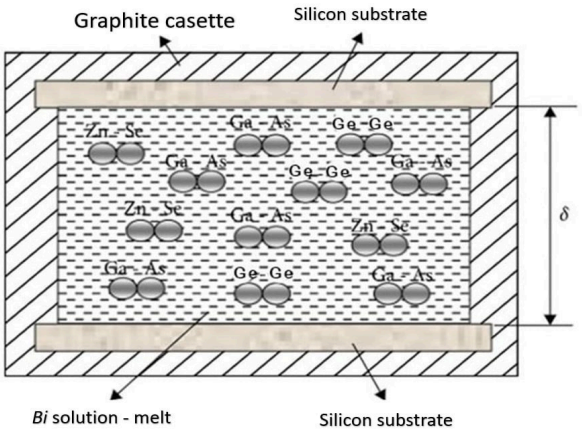

Figure 3: Diagram of component distribution in the melt solution between substrates at δ > 0.8 mm during crystallization.

To quantitatively assess the possibility of natural convection, the Rayleigh criterion (R_a) is used [15]:

$$R_a = \frac{g\beta\Delta T L^3}{\nu\alpha} \quad (2)$$

where: g—acceleration due to gravity, β—coefficient of volumetric thermal expansion, ΔT—temperature gradient in the melt, L—characteristic size (e.g., distance between substrates), ν—kinematic viscosity of the melt, α—thermal conductivity coefficient (thermal diffusion). Substituting characteristic values for the system under study ($g = 9.81$ m/s^2, $\beta = 1.2\cdot10^{-4}$ 1/K, $\Delta T = 100$ K, $L = 0.8$ mm, $\nu = 5\cdot10^{-7}$ m^2/s, $\alpha = 1\cdot10^{-7}$ m^2/s), we obtain: $R_a \approx 1206$. This value is significantly lower than the critical value $R_{ac} \approx 1700$ required for the stable development of natural convection. Consequently, at a gap of less than 0.8 mm, the dominant mass transfer mechanism in the system is molecular diffusion. However, when the gap is increased above 0.8 mm, it is possible to reach the critical value R_{ac}, which will lead to the development of natural convection. This contributes to the intensification of mass transfer to the upper crystallization front and, as a result, to the accelerated growth of films on the upper substrate. At the same time, the unevenness of mass transfer

can negatively affect the structural integrity of the films, leading to a deterioration in their crystalline quality. Thus, analysis of the conditions for the formation of boundary layers and evaluation of the Rayleigh criterion confirm that at small gaps (<0.8 mm), growth is regulated mainly by diffusion processes, while at larger gaps, convective mass transfer mechanisms begin to predominate [16].

To prepare the melt solution, the solubility of Ge_2, GaAs, and ZnSe in bismuth (Bi) was studied in the temperature range of 750–650°C. The experiment was conducted using the weight loss method, in which samples of Ge_2, GaAs, and ZnSe were immersed in liquid bismuth and held until the solution reached saturation [17]. At a temperature of 730°C, the composition of the Bi–Ge–GaAs–ZnSe melt was as follows: Bi—100 g, Ge—3 g, GaAs—2 g, ZnSe—1 g. Based on these data, it was hypothesized that at an epitaxy temperature of 750°C, Ge_2, GaAs, and ZnSe compounds exist in bismuth predominantly in molecular form. This assumption is confirmed by experimental results on the solubility of components in Bi. According to phase diagrams, the dissociation of Ge_2, GaAs, and ZnSe into separate atoms (Ga, As, Zn, Se) with their subsequent dissolution in bismuth proceeds similarly to the dissolution processes of pure elements. Despite the high melting points of Ga, As, Zn, and Se compared to Bi, the addition of a significant amount of bismuth significantly reduces the melting point of the entire system. Thus, at a temperature of 750°C, the multicomponent system is in a molten state, and its components exhibit high mutual solubility [18].

Fig. 4 shows the dependence of the solubility of Ge_2, GaAs, and ZnSe in bismuth (Bi) on temperature. Analysis of the experimental data shows that point defects form in the order $Ge_2 \rightarrow GaAs \rightarrow ZnSe$. This order corresponds to the principle of conservation of the total number of electrons involved in chemical bonds as the covalent radii of the substituting atoms decrease. In addition, a key condition for successful liquid-phase epitaxy is maintaining the melt solution in a supersaturated state.

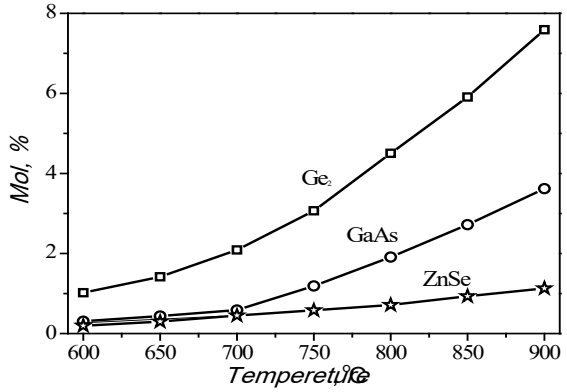

Figure 4: Temperature dependence of the solubility of Ge_2, GaAs, and ZnSe in Bi.

The observed growth of solid solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ under such conditions indicates that the bismuth-containing melt is saturated with stable Ga–As, Ge–Ge, and Zn–Se molecular complexes that do not dissociate into separate atoms. This confirms the applicability of the principle of similarity ("like dissolves like"): the formation of the crystalline phase begins with the crystallization of germanium upon reaching saturation with the corresponding compounds in the solution in the early stages of growth. A decrease in temperature leads to supersaturating of GaAs and ZnSe components, which creates favorable conditions for the crystallization of a solid solution $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$. To study the influence of technological parameters on the growth of GaAs, a series of experiments was conducted with the following conditions: gap between substrates: a = 0.8 mm, initial epitaxy temperature: T_1 = 750°C, final temperature: T_2 = 650°C, cooling rate: ϑ = 1°C/min. Solid solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ were grown at various combinations of these parameters, which made it possible to evaluate their influence on the morphology and structural quality of the resulting layers. Thus, reducing the gap contributed to the suppression of convective flows and the transition to molecular diffusion, which led to improved uniformity and reduced film defects. Increasing the initial epitaxy temperature (T_1) had a positive effect on the degree of crystalline

perfection due to the intensification of diffusion processes and a reduction in the probability of structural defects forming. At the same time, an excessively high cooling rate ($\vartheta > 1$°C/min) led to degradation of the film structure, which was due to an increase in the temperature gradient and the appearance of mechanical stresses that disrupted the integrity of the crystal lattice.

3 Conclusions

Experimental results confirming the possibility of growing solid solutions $(Ge_2)_{1-x-y}(GaAs_{1-\delta}Bi_\delta)_x(ZnSe)_y$ on silicon substrates using a Ge buffer layer are presented. Optimal technological conditions for obtaining structurally perfect epitaxial layers of this solid solution have been determined. The layers were obtained from a bismuth-containing melt by liquid-phase epitaxy. Epitaxial growth was carried out by forced cooling at a rate of 1°C/min in a palladium-purified hydrogen atmosphere. The layers were crystallized in the temperature range of 750–650°C. Experimental studies have shown that the growth of the epitaxial layer depends on the distance between the two substrates: as the gap increases, the stability of the crystal film formation decreases. The growth of the film on the upper and lower substrates critically depends on the size of the gap. Statistical analysis of the data obtained showed a symmetrical distribution of gaps with an average value of 0.8 mm and a spread of about 0.1 mm, which is due to the combined influence of diffusion and gravitational flow of the melt to the substrates oriented perpendicular to the vertical axis of the installation.

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Availability of Data and Materials: All data supporting the findings of this study are included in the article.

Ethics Approval: Not applicable. This study did not involve human or animal subjects.

Conflicts of Interest: The author declares no conflicts of interest to report regarding the present study.

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