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Growth GaInAsSbBi solid solution on misoriented GaSb(100) 6° (111)A substrate

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The paper presents the results of growing solid solutions of GaInAsSbBi by pulsed laser deposition on a misoriented GaSb(100) 6° (111)A substrate. The results of structural analysis using X-ray diffraction, transmission, electron and atomic force microscopy show that the main growth mechanism is the Volmer–Weber. The films have a polycrystalline structure. Stacking faults, twins and dislocations are present in the film volume. The composition of the films is determined by energy-dispersive microanalysis as $Ga_{0.75}In_{0.25}As_{0.87}Sb_{0.1}Bi_{0.03}$.

Keywords: III–V compounds, GaSb, gallium antimonide, solid solutions.

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Pulsed laser deposition is becoming increasingly popular for growing semiconductor thin films [1–6]. The main advantages of pulsed laser deposition (PLD) over other physical deposition methods are the ability to control the stoichiometry of films [7,8], a decrease in the temperature of the substrate for growing thin films III–V [9], and a discrete flow of matter from the target to the substrate in the intervals the time between laser pulses. At the moment, the main disadvantage of the method is the presence of droplets on the growth surface. At the time of writing, two cases of GaInAsSbBi growing on a GaSb substrate were known in 2022: molecular beam epitaxy [10] and PLD [11]. Generalized results of growing a GaInAsSbBi solid solution on a misoriented GaSb substrate using the PLD method will be presented in this study. The relevance of growing semiconductor films on GaSb substrates is due to the fact that they have a lattice parameter close to other compounds of groups III–V, and a narrow band gap allows them to create heterostructures in the mid-infrared range. Misoriented substrates are used in the growing of solid-state heterostructures to improve the structural quality of epitaxial layers [12,13]. The relevance of introducing Bi into solid solutions of groups III–V is due to the fact that in 2007 the effect of valence band anti-intersection was discovered when metalloids were added to GaAs [14], and then in 2013 the possibility of overcoming several fundamental disadvantages of light-emitting devices was theoretically predicted in the near and mid-infrared range caused by Auger recombination and spin-orbit splitting in the valence band [15]. In the same study, it was shown that compounds with Bi and Sb have the highest spin-orbit splitting energy, which shifts the valence band profile into the band gap, reducing it. Due to the large physical size of the bismuth atom, its compounds have been used in a new class of highly mismatched semiconductor alloys [16]. The above facts show the high practical relevance of developing such a class of semiconductor materials. In this regard, the aim of the work was to grow a GaInAsSbBi solid solution on a misoriented GaSb substrate using the PLD method and study its morphology and structural properties.

The samples were grown using the PLD method [11]. GaSb(Te)(100) plates oriented at 6° to the (111)A (GaSb(100) 6° (111)A) plane were used as the substrate. We have already obtained GaInAsSbBi polycrystalline films in Ref. [11], so in this experiment we decided to reduce the growth temperature to 300 °C in order to change the surface diffusion of growth elements. Based on the results obtained in Ref. [11] , sputtering was carried out from a target with $x_{\mathrm{Bi}} = 10$ at.%. The remaining growth parameters (pressure, laser fluence, deposition time) did not differ from those indicated in Ref. [11]. The study of structural properties and morphology was carried out using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM), as well as X-ray diffraction (XRD). The elemental analysis was performed by energy dispersive X-ray spectroscopy.

The results of the surface morphology study using SEM and AFM methods are shown in Figure 1. The images show the surface roughness characteristic of grown films and the presence of rare droplets on it, which are still inherent in the PLD method and are due to several factors: the presence of a strong surface-active effect of bismuth [17], the segregation of In, complex processes of surface diffusion, as well as a low melting point of Ga.

Based on the results of scanning the surface (Figure 1), it can be concluded that the GaInAsSbBi film grew in

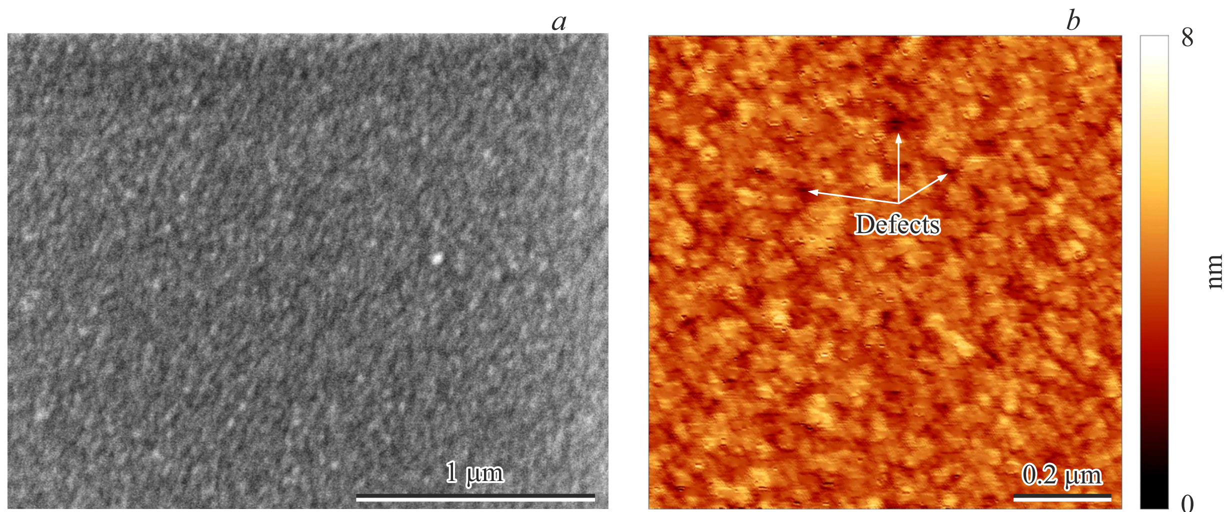

Figure 1. Morphology of the GaInAsSbBi film surface on a GaSb(100) substrate oriented by 6° to the plane (111)A: *a*) — SEM image; *b*) — 2D AFM image, $1 \times 1\,\mu m^2$.

the Vollmer–Weber's mode, i.e., the island growth mode. The output of packaging defects can be observed on the surface of the film in the AFM image (Figure 1, *b*). Elemental analysis by energy dispersive microanalysis showed that all the target elements (Ga, In, As, Sb, Bi) are present in the film. The film composition is defined as $Ga_{0.75}In_{0.25}As_{0.87}Sb_{0.1}Bi_{0.03}$. We reported in Ref. [11] achieving a concentration of 6 at.% Bi in GaInAsSbBi film, but we were unable to repeat this result in subsequent experiments with the same height configuration of the equipment.

Studies of the crystal structure of GaInAsSbBi films using XRD and TEM methods are shown in Figures 2 and 3, respectively.

Figure 2 shows the characteristic XRD spectrum of GaInAsSbBi films grown on a GaSb(100) substrate oriented at 6° to the (111)A plane. The shape of the XRD spectra corresponds to the polycrystalline structure of the material. This is evidenced by the large peak hemispheres and the high baseline background. The obtained XRD spectrum is integral and is due to both the presence of peaks of the GaSb substrate and the probable presence of phase inclusions. To indicate XRD peaks, the symbols in Figure 2 show the positions of the crystallographic planes allowed by the selection rule for the GaSb(100) [18] substrate and the GaSb(100) substrate oriented at 6° to the (111)A plane. The ideal lattice of compounds III–V is a face-centered cubic lattice, therefore planes with all even or all odd Miller indices were considered allowed. The position of the main peaks of reflection from the film is shifted relative to the peaks for both types of GaSb, which indicates a difference in the compositions of the film and the substrate and their lattice parameters. By comparing the angular positions of the XRD peaks (Figure 2) of the GaInAsSbBi/GaSb heterostructure with the ideal volumetric GaSb, it can be

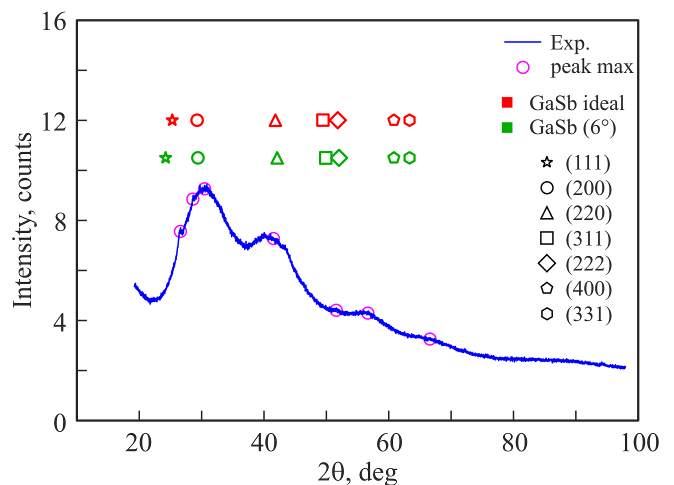

Figure 2. Diffraction pattern of heterostructure GaInAsSbBi/GaSb(100) 6° (111)A.

concluded that the main phase of the GaInAsSbBi film corresponds to the symmetry group $F\bar{4}3m$. Based on the analysis of ICCD PDF database cards [18], it was found that the most intense and broad peaks on the XRD curve with maxima $2\theta = 30.34361$, 41.35565, 56.50828 are formed by InGaAs, InSbBi, InAsSb, GaAsBi, GaSbBi, GaAsSb phases with lattice planes (111), (220), (311).

For a more detailed structural analysis, GaInAsSbBi/GaSb heterostructures were studied by the TEM method (Figure 3).

The TEM images (Figure 3, *a, b*) show phase inclusions and structural defects (packing defects, twins, dislocations) in the volume of the GaInAsSbBi film. Grain boundaries are perpendicular to the plane of the heterogeneous boundary. The grain size is comparable to the film

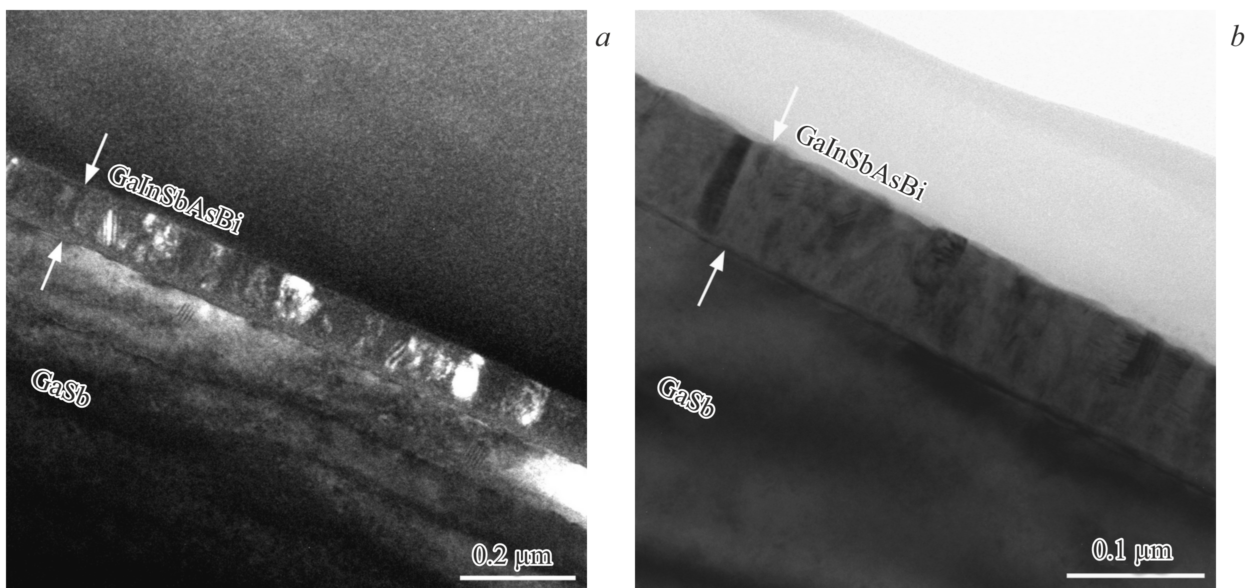

Figure 3. TEM images of the heterostructure GaInAsSbBi/GaSb(100) 6° (111)A: *a* — dark-colored; *b* — light-colored.

thickness. The characteristic thickness of the films reaches ~ 80 nm and is comparable to the one shown in Ref. [11]. A texture is visible on the surface of the film, which is confirmed by the AFM results (Figure 1, *b*). Based on the results of TEM, XRD, and AFM, it can be concluded that the $Ga_{0.75}In_{0.25}As_{0.87}Sb_{0.1}Bi_{0.03}$ film grows on a mismatched substrate GaSb(100) 6° (111)A occurs in the Vollmer–Weber mode.

Thus, thin films $Ga_{0.75}In_{0.25}As_{0.87}Sb_{0.1}Bi_{0.03}$ were grown by the PLD method on a mismatched substrate GaSb(100) 6° (111)A. It is shown that the films have a polycrystalline structure and contain phase inclusions. Growth occurs in the Vollmer–Weber mode. Reduction of the growth temperature on misoriented substrates GaSb(100) 6° (111) leads to an improvement in surface morphology, but it does not completely eliminate the polycrystallinity of GaInAsSbBi films with the same process equipment described in Ref. [11]. The results obtained above show that enhanced growth control in the PLD method will improve the crystalline properties of GaInAsSbBi solid solutions on misoriented GaSb substrates and realize epitaxial cultivation of highly mismatched semiconductor alloys based on III–V compounds doped with bismuth.

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Conflict of interest

The authors declare that they have no conflict of interest.

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