Technical Physics Letters, 2022, Vol. 48, No. 5

06.5;08.2

Structural properties of GaInAsSbBi solid solutions grown on GaSb substrates

© *A.S. Pashchenko*[1], *O.V. Devitsky*[1,2], *L.S. Lunin*[1], *M.L. Lunina*[1], *O.S. Pashchenko*[1]

[1] Southern Scientific Center, Russian Academy of Sciences, Rostov-on-Don, Russia
[2] Federal Research Center North-Caucasian Federal University, Stavropol, Russia
E-mail: as.pashchenko@gmail.com

Received February 14, 2022
Revised March 27, 2022
Accepted March 30, 2022

GaInAsSbBi solid solutions with different Bi contents are synthesized on *n*-GaSb substrates with a misorientation of 6° between the (100) and (111)*A* planes. Structural properties and morphology of GaInAsSbBi thin films are studied. Transmission electron microscopy and X-ray diffraction have shown that the films have a polycrystalline structure. It is found that an increase in the Bi concentration in the solid solution leads to a decrease in the average size of the region of coherent scattering by (111) reflection from 20 to 5 nm. It is shown that in films with a lower content of Bi, the thickness of the transition amorphous layer at the ?layer-substrate? heterointerface decreases.

Keywords: solid solutions, GaInAsSbBi, GaSb, III–V compounds.

DOI: 10.21883/TPL.2022.05.53481.19164

The most important structural element of modern nanoheterostructures for lasers, solar cells and photodiodes are potential barriers based on four and five-component solid solutions to create high carrier localization and transition buffer layers [1–4]. Heterostructures on GaSb substrates are of practical interest for mid- and far-infrared devices. The GaInAsSbBi solid solution is a good candidate for the mid-infrared range as already at 2% Bi an absorption edge of 5 μm at 120 K can be reached [5]. The relevance of the development of bismuth-containing solid solutions is due to the possibility of improving the microstructure of epitaxial layers due to the proximity of the covalent radii of Bi and some elements of groups III and V. Also, Bi is the largest low-toxicity group V element which drastically reduces the band gap width of III–V compounds to between 55–90 meV/% Bi [6]. In heteroepitaxy of solid solutions on binary substrates, the array mismatch between the thin film and the substrate, as well as the substrate misorientation [7] have a significant influence on the crystal structure and morphology of the deposited material. Previously, researchers have studied GaSb-based heterostructures that do not contain Bi [8–10]. The molecular beam epitaxy of GaInAsSb solid solution with Bi fraction of 0.13% on GaSb (100) substrates [5] has been known to be realized by now.

The aim of this work was to synthesize GaInAsSbBi solid solution on GaSb substrate and to study the effect of bismuth on its structural properties.

Solid solutions of $\mathrm{Ga}_z\mathrm{In}_{1-z}\mathrm{As}_{1-x-y}\mathrm{Sb}_y\mathrm{Bi}_x$ were grown in an experimental unit by pulsed laser spraying [11]. Growth was performed on *n*-GaSb substrates with 6° misorientation between planes (100) and (111)*A*. Residual pressure in the chamber was 10^{-4} Pa. AYG : Nd^{3+} laser with a wavelength of 532 nm (second harmonic) was used as the spraying source. For all samples, the substrate temperature was 350°C, laser energy density was $F = 2.3\,\mathrm{J/cm^2}$, deposition time was 60 min. To evaluate the Bi effect on the structural properties of the heterostructures, two targets with the calculated composition of $\mathrm{Ga_{0.85}In_{0.15}Sb_{0.1}As_{0.85}Bi_{0.05}}$ and $\mathrm{Ga_{0.85}In_{0.15}Sb_{0.1}As_{0.8}Bi_{0.1}}$ were manufactured. The structural properties were studied by X-ray diffraction (XRD) on a D8 Discover diffractometer (Bruker) in the $\theta-2\theta$-scanning mode using CuK_α radiation and by transmission electron microscopy (TEM) on a Jeol JEM-2100F microscope in the HAADF-STEM mode. The chemical composition of the solid solutions and Bi mapping across the film thickness was determined by X-ray energy dispersive simulation (EDS).

Figure 1 shows TEM images of GaInAsSbBi/GaSb heteroboundaries grown from targets with different Bi contents. It can be seen that the film is predominantly made up of randomly oriented grains. A distinctive feature of the films grown is the presence of a transitional amorphous layer at the hetero-boundary and amorphous phase inclusions in the films. In Fig. 1, *a* ($x_{\mathrm{Bi}} = 5$ at.%) the thickness of the transition layer is about 3 nm. For a sample grown from a target with $x_{\mathrm{Bi}} = 10$ at.% (Fig. 1, *b*), the thickness of the transition layer reaches 5 nm. In both cases, a grain structure of GaInAsSbBi films can be observed, indicating the predominance of polycrystalline structure. The insets to Fig. 1, *a*, *b* show TEM images of cross sections of GaInAsSbBi films grown from targets with $x_{\mathrm{Bi}} = 5$ and 10 at.%, respectively. For a target $x_{\mathrm{Bi}} = 5$ at.% the film thickness reaches about 40 nm and for $x_{\mathrm{Bi}} = 10$ at.% — about 80 nm. In both cases, the grain size in the growth direction is comparable to the thickness of the films (insets in Fig. 1, *a*, *b*).

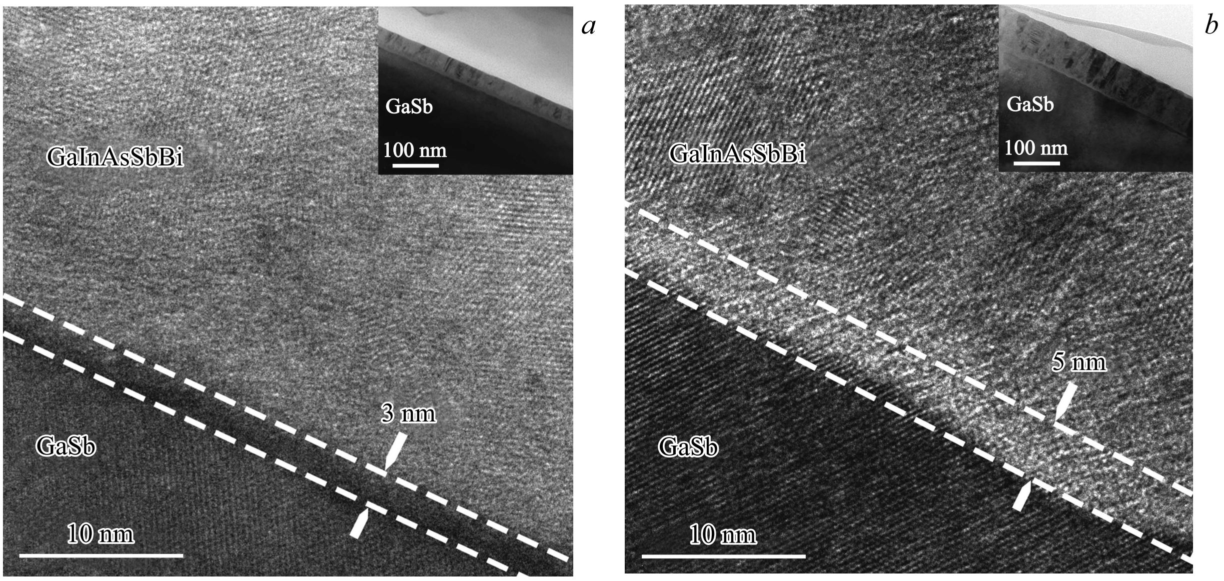

Figure 1. TEM images of GaInAsSbBi/GaSb hetero-boundaries grown from targets with different Bi contents: $x_{\mathrm{Bi}} = 5$ (*a*) and 10 at.% (*b*).

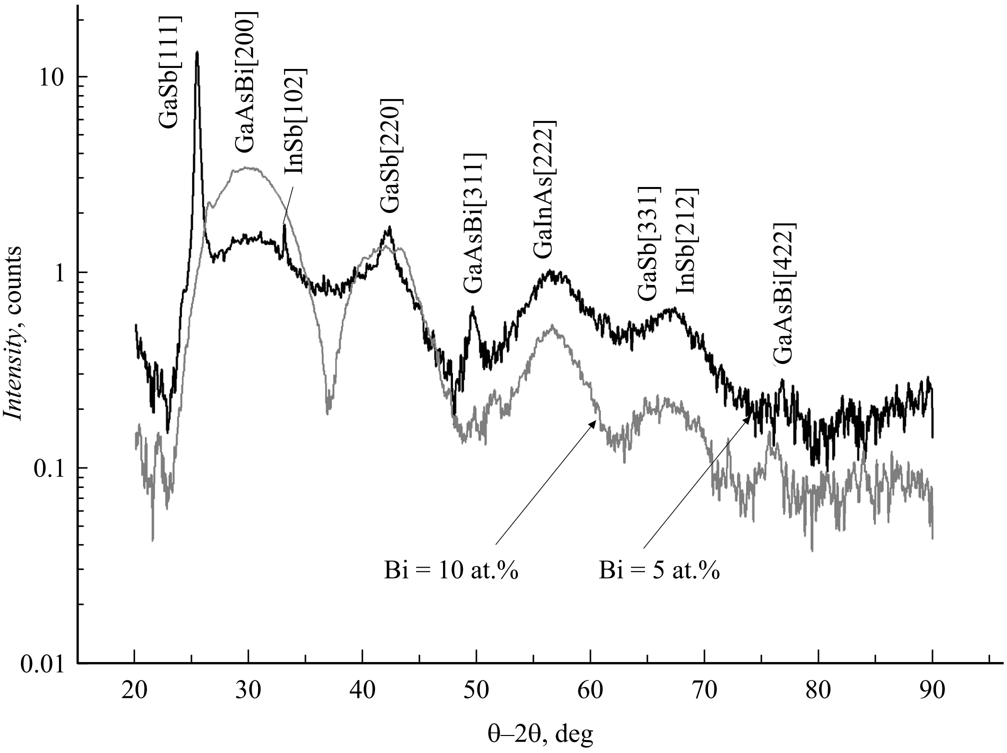

Figure 2. XRD spectra of GaInAsSbBi/GaSb heterostructures grown from targets with different Bi contents.

X-ray microstructural analysis and elemental analysis were carried out to obtain more detailed information on the structural properties of the grown solid solutions and to confirm the Bi inclusion in the film composition and volume. Figure 2 shows the results of the microstructural analysis carried out by XRD in the $\theta-2\theta$ geometry. The measured curves show multiple reflexes caused by reflections from different crystallographic directions which testifies to the polycrystalline structure of GaInAsSbBi films grown. For the curve corresponding to the film obtained from a target with $x_{\mathrm{Bi}} = 5$ at.%, it was found that the main phase corresponds to a cubic sphalerite type structure. The crystalline components of the film are represented by two spatial groups $F\bar{4}3m$ with different cell parameters. The average size of the coherent scattering region (CSR) calculated from reflection (111) is 20 nm. In addition, an amorphous phase is detected in the film structure, which is also confirmed by Fig. 1, *a*. In the case of $x_{\mathrm{Bi}} = 10$ at.%

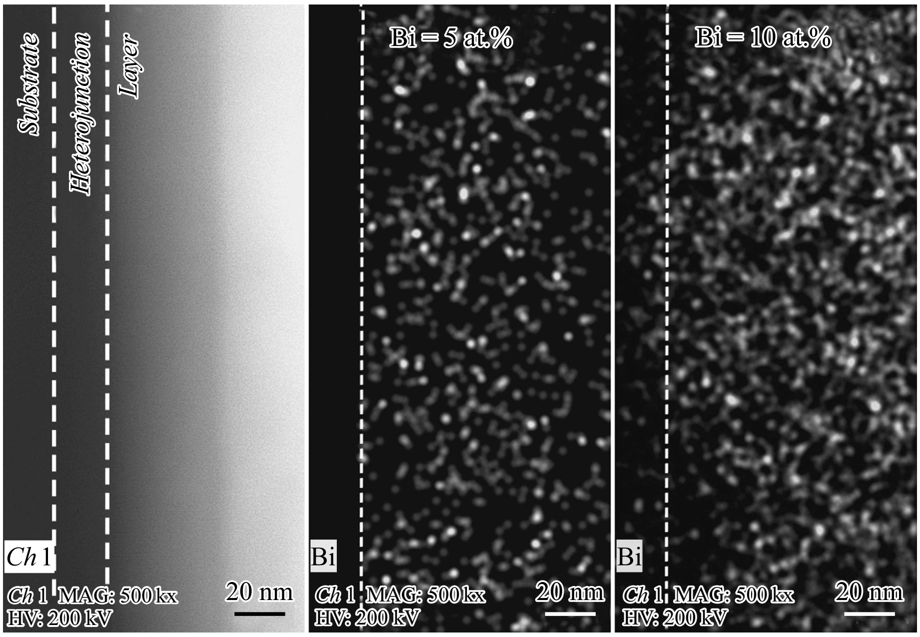

Figure 3. TEM-image of GaInAsSbBi/GaSb hetero-boundary section (left) and EDS-STEM maps of Bi distribution in GaInAsSbBi layer (center and right).

(Fig. 2) the main phase also corresponds to a sphalerite-type cubic structure. The average CSR size calculated from reflection (111) is less than 5 nm. The main crystal phases forming the structure of the GaInAsSbBi films grown are GaSb, InSb, $GaAs_{0.5}Bi_{0.5}$.

One of the important tasks of the current study was to establish the Bi incorporation into the solid solution and its distribution over the layer thickness. The elemental composition of the grown GaInAsSbBi films and Bi mapping by layer thickness were determined by the EDS method. Figure 3 shows the TEM image (HAADF-STEM) and Bi distribution maps (EDS-STEM) obtained in sample drift compensation mode during exposure. The mapping results show that for targets with $x_{\mathrm{Bi}} = 5$ and 10 at.%, there is a different distribution of Bi in the hetero-boundary region. In the case $x_{\mathrm{Bi}} = 5$ at.% the film boundary is sharper compared to $x_{\mathrm{Bi}} = 10$ at.%. We believe this is due to a thinner amorphous transition region (Fig. 1, *a*), which changed the kinetics of surface diffusion of elements, slowing its speed. For the case $x_{\mathrm{Bi}} = 10$ at.% the growth rate of the layer was found to be 2 times higher, as confirmed by Fig. 1, *a*, *b*. The composition of the films grown was determined from the EDS results: $Ga_{0.75}In_{0.25}Sb_{0.1}As_{0.87}Bi_{0.03}$ ($x_{\mathrm{Bi}} = 5$ at.%) and $Ga_{0.83}In_{0.17}Sb_{0.08}As_{0.86}Bi_{0.06}$ ($x_{\mathrm{Bi}} = 10$ at.%). It should be noted that the composition data obtained are semi-quantitative in nature as the GaSb substrate is strongly influenced by the X-ray beam energy of 20 keV and the small thickness of the films (less than 100 nm).

Thus, the study of structural properties of GaInAsSbBi solid solutions grown on misoriented *n*-GaSb substrates has shown that the films have polycrystalline structure in which the main phase corresponds to the cubic sphalerite-type structure. The results of X-ray microstructural analysis showed that the main phases forming the thin film are GaSb, InSb and $GaAs_{0.5}Bi_{0.5}$. It is found that increasing the Bi fraction in the composition of the films grown from 3 to 6 at.% leads to a decrease in the average size of the CSR by reflection (111) from 20 to 5 nm. In addition, an increase in Bi concentration on the growth surface was found to change the kinetics of growth processes towards an increase in growth rate. In GaInAsSbBi thin films with high Bi content, the thickness of transition amorphous layer is larger (Fig. 1), which seems to be caused by an increase of array parameters mismatch between the layer and the substrate arrays. The study results show that GaInAsSbBi solid solutions with $x_{\mathrm{Bi}} < 5$ at.% grown on misoriented GaSb substrates have promise for use as transition buffer layers in semiconductor nano-heterostructures.

Acknowledgments

The studies were performed using the equipment of the Federal Common Research Center „Materials Science and Diagnostics in Advanced Technologies“, supported by the Ministry of Education and Science of Russia (unique project identifier: RFMEFI62119X0021).

Funding

The structures were grown and studied with financial support by the Russian Science Foundation (Grant № 19-79-10024).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] H. Sugiyama, K. Uchida, X. Han, G.K. Periyanayagam, M. Aikawa, N. Hayasaka, K. Shimomura, J. Cryst. Growth, **507**, 93 (2019). DOI: 10.1016/j.jcrysgro.2018.10.024

[2] F.I. Zubov, M.E. Muretova, L.V. Asryan, E.S. Semenova, M.V. Maximov, A.E. Zhukov, J. Appl. Phys., **124**, 133105 (2018). DOI: 10.1063/1.5039442

[3] S. Ilahi, N. Yacoubi, F. Genty, Opt. Mater., **69**, 226 (2017). DOI: 10.1016/j.optmat.2017.04.050

[4] N. An, L. Ma, G. Wen, Z. Liang, H. Zhang, T. Gao, C. Fan, Appl. Sci., **9**, 162 (2019). DOI: 10.3390/app9010162

[5] R.A. Carrasco, C.P. Morath, J.V. Logan, K.B. Woller, P.C. Grant, H. Orozco, M.S. Milosavljevic, S.R. Johnson, G. Balakrishnan, P.T. Webster, Appl. Phys. Lett., **120**, 031102 (2022). DOI: 10.1063/5.0078809

[6] L. Wang, L. Zhang, L. Yue, D. Liang, X. Chen, Y. Li, P. Lu, J. Shao, S. Wang, Crystals, **7**, 63 (2017). DOI: 10.3390/cryst7030063

[7] C.A. Wang, C.J. Vineis, D.R. Calawa, MRS Proc., **794**, T9.6 (2003). DOI: 10.1557/PROC-794-T9.6

[8] H.-W. Cheng, Sh.-Ch. Lin, Z.-L. Li, K.-W. Sun, Ch.-P. Lee, Materials, **12**, 317 (2019). DOI: 10.3390/ma12020317

[9] Y.L. Casallas-Moreno, G. Villa-Martínez, M. Ramírez-Lopez, P. Rodríguez-Fragoso, M.L. Gomez-Herrera, M. Perez-Gonzalez, A. Escobosa-Echavarría, S.A. Tomas, J.L. Herrera-Perez, J.G. Mendoza-Alvarez, J. Alloys Compd., **808**, 151690 (2019). DOI: 10.1016/j.jallcom.2019.151690

[10] L.A. Sokura, Ya.A. Parkhomenko, K.D. Moiseev, V.N. Nevedomsky, N.A. Bert, Semiconductors, **51**, 1101 (2017). DOI: 10.1134/S1063782617080310.

[11] A.S. Pashchenko, O.V. Devitsky, L.S. Lunin, I.V. Kasyanov, D.A. Nikulin, O.S. Pashchenko, Thin Solid Films, **743**, 139064 (2022). DOI: 10.1016/j.tsf.2021.139064