International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/140208

Structural Features and Electrical Properties of $Ge_{1-x}Sn_x$ Solid Solutions Grown on Ge, GaAs Substrates

A. Sh. Razzokov

Department of Physics, Faculty of Science, Urgench State University, 14, Kh. Alimdjan str, Urgench City, 220100, Uzbekistan

Received: 25 Jul. 2024, Revised: 11 Jan. 2025, Accepted: 18 Feb. 2025.
Published online: 1 May 2025

Abstract: In this article single-crystal films of the $Ge_{1-x}Sn_x$ solid solution from a limited tin solution-melt in the temperature range of 893-723 K at a cooling rate of 0.5-1.5 K/min on an EPOS installation were grown epitaxial layers of $Ge_{1-x}Sn_x$ on Ge(111) and GaAs(100) substrates with carrier concentration $n=(1\div5)\cdot10^{17}cm^{-3}$, $n=(4\div7)\cdot10^{17}cm^{-3}$, respectively. The gap between the substrates was 0.65÷1.2 mm. Technological conditions have been achieved for obtaining a GaAs- $Ge_{1-x}Sn_x$ heterostructure with a smooth substrate-film boundary, with the supercooling temperature being T=6.2 °C. The single crystallinity of the $Ge_{1-x}Sn_x$ $(0 \le x \le 0.03)$ film was determined by X-ray diffraction. The photosensitivity of the film covers the spectral region of 0.5-1.9 eV.

Keywords: epitaxial layer, heterostructure, solid solution, hypothermia.

1. Introduction

Currently, one of the important and open problems of sputtering physics is still the presence of emission sputtering products of multimolecular clusters [1-3]. The very nature of the processes underlying the formation of clusters during sputtering remains largely unclear. This moment the collision cascade model during sputtering is one of the main models explaining this process. However, how and how the clusters leave the surface can be different.

The growth of semiconductor solid solutions is of undoubted interest for the development of modern semiconductor instrumentation, since a solid solution synthesized from several semiconductor components can combine the advantages of each of them. It should be noted that expanding the photosensitivity spectrum of semiconductors in the IR region is one of the pressing problems of instrument engineering [1, 2]. One of these materials is $Ge_{1-x}Sn_x$ solid solutions covering the spectral region of the Ge range and below. $Ge_{1-x}Sn_x$ semiconductor alloy is attractive for mid-infrared photodetector applications due to its narrow bandgap. Therefore, $Ge_{1-x}Sn_x$ is promising for the manufacture of photodetectors and laser devices in the near and mid-infrared range [3,4]. In [5], using low-temperature molecular beam epitaxy, it was possible to grow $Ge_{1-x}Sn_x$ films on Ge/AlAs/Al_2O_3 substrates. However, XRD study shows that the grown samples have tetragonal deformation. The presence of twins increased significantly for the sample grown with a higher chemical content of Sn (5.2%) compared to the sample grown with 3.6% Sn. By growing a much thicker layer, it was possible to suppress the presence of defects in the epitaxial layers. To obtain crystalline perfect $Ge_{1-x}Sn_x$ layers, InP(001) substrates were used. It was possible to grow Ge1-xSnx using low-temperature molecular beam epitaxy at growth temperatures of 70 and 100 °C with a composition x ~ 0.25. However, during the heteroepitaxy of $Ge_{0.75}Sn_{0.25}$, $Ge_{1-x}Sn_x$ regions with a low Sn content are locally formed. TEM analysis has shown that low-tin $Ge_{1-x}Sn_x$ is formed by agglomeration of tin to form In-Sn alloys [6]. In work [7] presented the growth of Ge and GeSn at growth temperatures of 500–600 °C on GaAs (001) substrates using two different buffer layers consisting of Ge/GaAs and Ge/AlAs using molecular beam epitaxy. The quality of Ge layers was studied using X-ray diffraction, atomic force microscopy, and photoluminescence methods. Using a Ge buffer layer, the direct transition shifted after the indirect transition to a longer wavelength region, which allowed the authors to suggest the presence of a GeSn material with a direct bandgap. $Ge_{1-x}Sn_x$ films with a thickness of 100 nm were also obtained by magnetron sputtering in the temperature range of 220–330 K. Studies of the Seebeck coefficients (α) and power coefficients show that, at $0.09 \le x \le 0.15$ in the chemical content range, the films have high meanings. However, the low electrical conductivity of the films complicates its application in the field of thermoelectricity. However, using dopings, $Ge_{1-x}Sn_x$ is interesting for complementary metal oxide semiconductors [8]. In order to develop high-performance short-wavelength infrared photonic devices based on low-dimensional group IV structures containing tin, $Ge_{0,883}Sn_{0,117}$/Ge was grown by molecular beam epitaxy under rapid thermal annealing (RTA) conditions. Analyzes of XRD, TEM, AFM, Raman studies show that

*Corresponding author E-mail: a.razzokov777@gmail.com

the GeSn/Ge structure maintains coherent deformation at a temperature of 400 °C and the sensitivity of the sample is improved by 4.15 and 3.78 times at wavelengths of 1.55 and 2.0 μm, respectively. However, at higher annealing temperatures, Sn segregation and Ge interdiffusion occur [9]. From the point of view of manufacturing optical devices, it is very important to obtain a direct-gap semiconductor material. To obtain GeSn alloys with a direct band gap (for Sn concentrations above 8%), the authors of [10], which have an indirect band gap, doped Ge with the semimetal Sn (E = -0.41 eV). Ge-buffered Si substrates were used as templates for epitaxy of GeSn layers and mitigated the lattice parameter mismatch between GeSn and Ge, Si (a_{Sn} = 0.6489 nm, a_{Ge} = 0.5658 nm, and a_{Si} = 0.5431 nm). They are first seeded with ~0.1 μm thick Ge at 400°C on a Si(001) substrate, then coated with ~2.4 μm Ge at 750°C. However, short-term thermal cycling at temperatures from 750 °C to 875 °C led to the appearance of threading dislocations. We have also shown the possibility of growing from the liquid phase on gallium arsenide substrates crystalline perfect epitaxial layers of solid solutions $(Sn_2)_{1-x}(InSb)_x$ ($0<x<0.95$) with a narrow width band gap E_g = 0.11 ÷ 0.12 eV in the growth temperature range 598÷533 K [11,12]. The main difficulty in obtaining high-quality structures of such composition was the difference in the lattice parameters of the substrate (a_{GaAs} = 0.5654 nm) and the film ($a_{(Sn2)1-x(InSb)x}$ = 0.6486 nm), which negatively affected the electrophysical and photoelectric properties. Therefore, of particular interest are the possibilities of synthesizing semiconductor solid solutions with a high degree of perfection based on the best-studied narrow-gap materials. From the above, we can say that to obtain crystalline perfect $Ge_{1-x}Sn_x$ solid solutions, quite a lot of theoretical and experimental work has been presented in the literature, and significantly successful results have been obtained. However, obtaining $Ge_{1-x}Sn_x$ single crystals with high tin contents (x>0.01) is difficult due to the inclusion of an insufficient amount of tin in the solid solution and the growth of epitaxial layers oriented in the direction of the substrate. In this work, the principles of obtaining $Ge_{1-x}Sn_x$ solid solutions and GaAs-$Ge_{1-x}Sn_x$ Ge-$Ge_{1-x}Sn_x$ structures based on them were studied. A study of some of their structural, electrophysical, and photoelectric properties was carried out. Taking into account the similar values of the lattice parameters of the GaAs and germanium compound (a_{GaAs} = 0.5654 nm, a_{Ge} = 0.5658 nm), as well as the similar values of their thermal expansion coefficients (α_{GaAs} = 5.93 10-6 K- 1; α_{Ge} = 6.1·10-6 K-1) of great interest is the production of GaAs-$Ge_{1-x}Sn_x$ heterostructures (0<x< 0.03), although the indicated base materials have different band gaps (ΔE_{GaAs} = 1.43 eV; ΔE_{Ge} = 0.67 eV) [13,14]. It should be noted that a small amount of Sn (0<x<0.03) in the chemical composition of the $Ge_{1-x}Sn_x$ solid solution does not significantly affect the values of the lattice parameters and the coefficient of thermal expansion of epitaxial layers, however, leads to a shift in the photosensitivity of the film to the IR region [15].

2. Method and results

We have studied the process of water film sputtering, which contains Na^+ ions in its composition. This process is a very interesting mechanism for sputtering molecules and atoms in the form of large clusters. The sodium ion located inside the film forms ionic bonds with its molecules. These bonds primarily depend on the charge of the ion. i.e., if the ion is positive, then negative molecular components accumulate around it, or vice versa. In our simulation, we used method of molecular dynamics. Numerical solutions of Newton's equations for interacting with particles is the basis of the method of molecular dynamics. This method often uses the Lennard-Jones potential. Epitaxial films were grown using a vertical-type quartz reactor with horizontally located substrates. To prevent the entry of uncontrolled impurities from the atmosphere into the reactor, the process of growing epitaxial layers was carried out in a hydrogen atmosphere. The composition of the melt solution, consisting of Ge and Sn, was determined from the state diagrams of Sn–Ge binary alloys. To prepare a liquid melt solution, the literature data described in [16-18] were used. 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 (Ge) and 350-400 μm (GaAs). To obtain a certain composition of the melt solution based on a tin solvent, germanium powders were used. The surface morphology of the grown films was studied using scanning electron microscopy (SEM EVO MA 10 (Zeiss)). Structural-phase studies were carried out on high-resolution diffractometers D2 PHASER/Bruker (GID and GONIO modes using HR-XRD, Panalytical/Empyrean). Specific resistance, mobility and concentration of the main charge carriers were determined using an HMS-5500 installation (Hall effect measurement system). The spectral characteristics of the samples were measured using a monochromator with a slit diameter of 0.2 mm.

3. Experimental and Discussion

Based on the above, from a tin solution-melt in a temperature range of 893-723 K with a cooling rate range of 0.5-2 K/min $Ge_{1-x}Sn_x$ epitaxial layers were grown on an EPOS installation. The substrates were Ge(111) and GaAs(100) plates with carrier concentration $n=(1\div5)\cdot10^{17}$ cm^{-3}, $n=(4\div7)\cdot10^{17}$ cm^{-3}, respectively, of donor conductivity type. The diameter and thickness of the substrate were 50 mm (Ge) and 350-400 μm (GaAs). The composition of the Sn + Ge melt solution, and the corresponding growth temperature range corresponded to those described in [19]. The composition of the $Ge_{1-x}Sn_x$ solid solution and the distribution of components in the grown epitaxial layers are studied and presented in Fig. 1

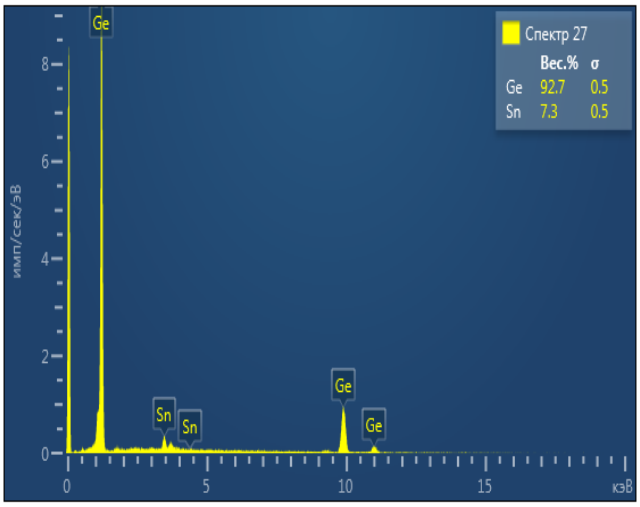

Fig. 1: Energy spectrum of the surface of $Ge_{1-x}Sn_x$ epitaxial layers obtained from a melt solution on a Ge substrate

The most optimal cooling rate for obtaining mirror-smooth layers of the $Ge_{1-x}Sn_x$ solid solution turned out to be 0.5-1.0 K/min, which corresponded to the actual cooling rate Stallization of layers 0.13-0.2 μm/min. The structural perfection of the grown layers, other things being equal, also depended on the size of the gap between the horizontally located substrates. The most optimal cooling rate for obtaining the most structurally perfect layers of solid solutions both on the upper and lower substrates were grown at gap values δ lying in the interval 0. 65÷1.2 mm. At values of δ>1.2 mm, the quality of the layers grown on the lower and upper substrates varied greatly, and the quality of the layers grown on the lower substrates was always higher than on the upper ones [20]. Qualitative assessment of the distribution of solution-forming components over the thickness of Ge–$Ge_{1-x}Sn_x$ and epitaxial films GaAs–$Ge_{1-x}Sn_x$ indicated an almost uniform distribution of components (Figs. 2, 3).

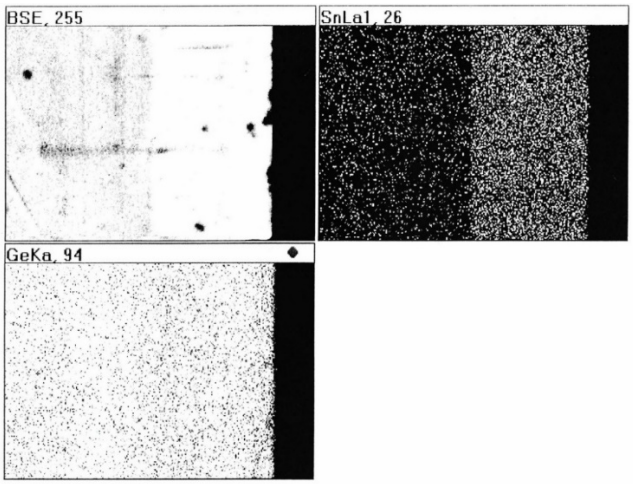

Fig. 2: Distribution of components and microstructure of the cross section of the Ge–Ge_{1-x} Sn_x epitaxial film (x = 0.03)

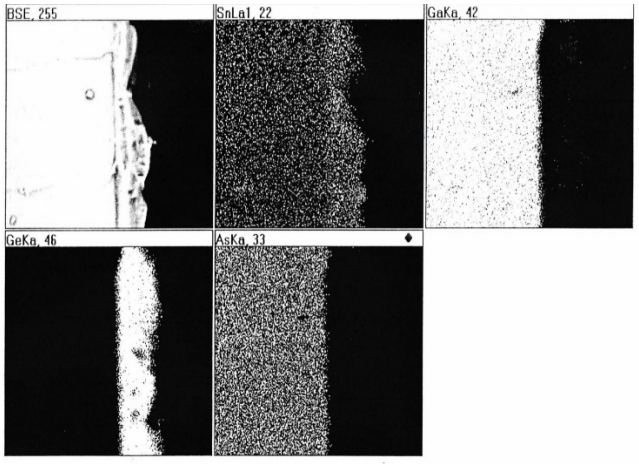

Fig. 3: Distribution of components and microstructure of the cross section of the GaAs-$Ge_{1-x}Sn_x$ epitaxial film (x = 0.03)

$Ge_{1-x}Sn_x$ epitaxial films are grown from a Ge + Sn melt solution onto a Ge substrate without technological difficulties due to the saturation of the liquid phase relative to Ge; this prevents melting of the surface layer of the substrate-film interface at the crystallization front. If growth is carried out on a "foreign" GaAs substrate, then due to the unsaturation of the Ge + Sn system of the solution-melt relative to GaAs, the substrate will lead to dissolution. 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. Based on theoretical calculations, the supercooling temperature for the solution-melt of the Ge + Sn system was determined in advance and applied in the technological growth process. It has been established that when growing a $Ge_{1-x}Sn_x$ solid solution on a GaAs substrate from the liquid phase, the optimal supercooling temperature is ΔT= 6,2°C. Thus, the technological conditions for obtaining a GaAs- $Ge_{1-x}Sn_x$ heterostructure with crystalline perfection and a smooth substrate-film interface have been achieved. Analysis of raster patterns and morphological studies of $Ge_{1-x}Sn_x$ solid solutions showed that defects appearing at the substrate-film interface depend on the value of x. The difference between the lattice parameters of the first crystallizing layer and the substrate is maximum. The relaxation of the significant coherent stresses that arise as a result leads to the formation of dislocations. With the growth of subsequent epitaxial layers, this difference decreases, since the role of the substrate is already played by the first formed film layer, in which the difference between the values of its lattice parameter and the second layer will already be smaller than in the previous case, and so on. As a result, a heterointerface is formed, the thickness and perfection of which can be controlled by changing growth regimes. It was found that with increasing tin content in the $Ge_{1-x}Sn_x$ solid solution, the structural perfection of the layers sharply deteriorates and even precipitates of the second phase

appear. Crystalline perfection and changes in lattice parameters of the solid solution were studied using the XRD method (Fig. 4). Precision measurements of the lattice parameters of the substrate and the grown film differed slightly (a_{Ge} = 0.5656 nm, $a_{Ge1-xSnx}$ = 0.5681 nm), and the absence of other diffraction maxima indicated the single-crystallinity of the resulting epitaxial layers.

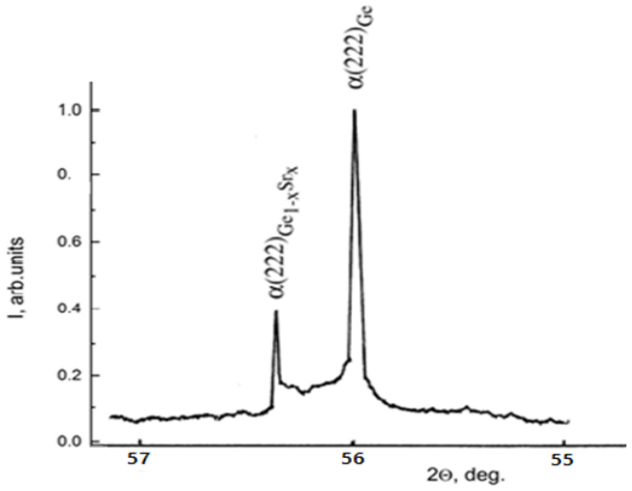

Fig. 4: Diffraction maxima (222) from lattices (Ge) and the Ge-$Ge_{1-x}Sn_x$ solid solution (x = 0.03)

Subsequently, some electrical properties of the resulting films were studied: the resistivity, Hall mobility and charge carrier concentration at a temperature of 300 K were determined: $\rho = \rho = (3\div7)\cdot10^{-2}$Ohm·cm, μ_p = 50÷110 $cm^2/V\cdot s$, $n_p = (5\div7)\cdot 10^{18}$ cm^{-3}. The films had hole type conductivity. Gold ohmic contacts were deposited onto $Ge_{1-x}Sn_x$ epitaxial layers and GaAs-$Ge_{1-x}Sn_x$ structures by vacuum deposition and their photoelectric properties were measured. The photosensitivity of the nGaAs-p$Ge_{1-x}Sn_x$ structure was measured in photodiode mode, illuminating the samples from the film side at a temperature of 300 K (Fig. 5). The photosensitivity of heterostructures covered a fairly wide range of the spectrum: from 0.5 eV to 1.9 eV, having two maxima (0.65 eV and 1.43 eV), which are associated with the band gap of the $Ge_{1-x}Sn_x$ solid solution and the contact region of the p-n junction of nGaAs-p$Ge_{1-x}Sn_x$ structures. Short-wave quanta are partially absorbed in the upper layers of the film. Photons that have penetrated the outer layers of the solid solution are absorbed already in the contact region, reaching the p-n junction of the nGaAs-p$Ge_{1-x}Sn_x$ structures. The shift in the photosensitivity range of the structures to a longer wavelength region of the spectrum (0.5 eV) is probably due to the presence of Sn in the composition of the $Ge_{1-x}Sn_x$ films. Despite the narrow band gap of the grown $Ge_{1-x}Sn_x$ films relative to the GaAs substrate, photon energy tunnels when the heterostructure is illuminated from the film side. The penetration of photons through a thin $Ge_{1-x}Sn_x$ (d=4÷6 μm) epitaxial layer onto the nGaAs-p$Ge_{1-x}Sn_x$ region (substrate-film) of the heterojunction creates a photovoltage in the infrared region of the spectrum.

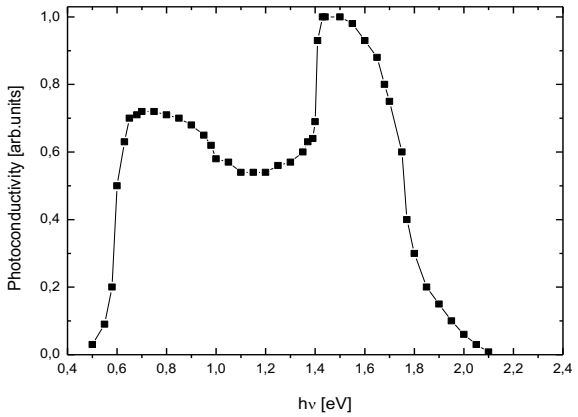

Fig. 5: Photosensitivity of the nGaAs-p$Ge_{1-x}Sn_x$ structure in photodiode mode at a temperature of 300 K.

4. Summary

Thus, the possibility of growing crystalline perfect epitaxial layers of solid solutions from a limited tin solution-melt has been demonstrated. $Ge_{1-x}Sn_x$ cores ($0 \le x \le 0.03$) 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 + Sn system was predetermined, which is equal to ΔT = 6.2 °C. The technological conditions for obtaining a solution-melt of GaAs-$Ge_{1-x}Sn_x$ heterostructures from the Sn-Ge system without sub-dissolution of the "foreign" substrate using supercooling have been established experimentally. The photosensitivity of heterostructures covered a fairly wide range of the spectrum: from 0.5 eV to 1.9 eV, having two maxima (0.65 eV and 1.43 eV), which are promising for use in the IR spectrum.

References

[1] Ch. Tan, S.Ke, J.Lv, Y.Huang, D.Peng, Zh.Duan, Y.Wu, J.Yang, F.Lin, Ch.Wang. Growth of single-crystalline GeSn films with high-Sn content on InP substrates by sputtering and rapid thermal annealing. *Applied Surface Science*.V.657, 2024, 159707. https://doi.org/10.1016/j.apsusc.2024.159707 .

[2] N. Taoka, G.Capellini, V.Schlykow, M.Montanari, P.Zaumseil, O.Nakatsuka, Sh. Zaima, Th.Schroeder. Electrical and optical properties improvement of GeSn layers formed at high temperature under well-controlled Sn migration. *Materials Science in Semiconductor Processing*.V.70, 2017, P. 139-144. https://doi.org/10.1016/j.mssp.2017.07.013.

[3] Y. Wang, L.Zhang, Z.Huang, Ch.Li, S.Chen, W.Huang, J.Xu, J.Wang. Crystallization of GeSn thin films deposited on Ge(100) substrate by magnetron sputtering. *Materials Science in Semiconductor Processing*.V.88, 2018, P.28-34. https://doi.org/10.1016/j.mssp.2018.07.030.

[4] H. Groiss, M.Glaser, M.Schatzl, M.Brehm, D.Gerthsen, D.Roth, P.Bauer, F. Schäffler. Free-running Sn precipitates: an efficient phase separation mechanism for metastable $Ge_{1-x}Sn_x$ epilayers. *Scientific Reports*, V.7, 2017, 16114. https://doi.org/10.1038/s41598-017-16356-8.

[5] Gayakwad, D.Singh, R.Kumar, Y.I.Mazur, Sh.Q.Yu, G.J.Salamo, S.Mahapatra, K.R.Khiangte. Epitaxial growth of $Ge_{1-x}Sn_x$ on c – Plane sapphire substrate by molecular beam epitaxy. *Journal of Crystal Growth*. V.618, 2023, 127306. https://doi.org/10.1016/j.jcrysgro.2023.127306

[6] Sh. Shibayama, K.Takagi, M.Sakashita, M.Kurosawa, O.Nakatsuka. $Ge_{1-x}Sn_x$ layers with x~0.25 on InP(001) substrate grown by low-temperature molecular beam epitaxy reaching 70 °C and in-situ Sb doping. *Materials Science in Semiconductor Processing*. V 176, 2024, 108302. https://doi.org/10.1016/j.mssp.2024.108302

[7] C. Gunder, F.Maia de Oliveira, E.Wangila, H.Stanchu, M.Zamani-Alavijeh, S. Ojo, S.Acharya, A.Said, Ch.Li, Y.I. Mazur, Sh.Q.Yu, G.J. Salamo. The growth of Ge and direct bandgap $Ge_{1-x}Sn_x$ on GaAs (001) by molecular beam epitaxy. *RSC Advances*.V.14, Iss.2, 2024, P.1250-1257. https://doi.org/10.1039/d3ra06774b.

[8] A. Portavoce, H.Khelidj, N.Oueldna, S.Amhil, M.Bertoglio, D.Mangelinck, L. Essaleh, K.Hoummada. Thermoelectric power factor of $Ge_{1-x}Sn_x$ thin films. *Materialia*. V.14, 2020, 100873. https://doi.org/10.1016/j.mtla.2020.100873.

[9] H. Zhao, G.Lin, Ch.Han, R.Hickey, T.Zhama, P.Cui, T.Deroy, X.Feng, Ch.Ni, Y.Zeng. Improving the short-wave infrared response of strained GeSn/Ge multiple quantum wells by rapid thermal annealing. *Vacuum*. V.210, 2023,111868. https://doi.org/10.1016/j.vacuum.2023.111868.

[10] J. M. Hartmann, T. Marion. Impact of flows, temperature and pressure on the GeSn growth kinetics with a digermane and tin tetrachloride chemistry. *Materials Science in Semiconductor Processing*.V.169, 2024, 107893. https://doi.org/10.1016/j.mssp.2023.107893.

[11] A. S.Saidov, A.Sh.Razzokov, D.V.Saparov. Preparation of epitaxial layers of the $(Sn_2)_{1-x}(InSb)_x$ solid solution from the liquid phase. *Letters to the Technical Physics*. –2002. –T. 28. – No.22. – P.7-10.

[12] A. Sh.Razzokov, U.P.Asatova, Sh.K. Ismoilov. Synthesis of three-component solid solutions $(Sn_2)_x(InSb)_{1-x}$. *Materials of the Republican scientific and technical conference with the participation of foreign scientists "Composite materials: Structure, properties and application*". Tashkent. – 2008. – P.136-138.

[13] Liu H., Jin Y. MOCVD Ge-on-GaAs and Its p-Type Doping via Incorporating Ga Atoms. *Procedia engineering*. – 2017. – Vol. 215. – P. 17-23.

[14] Kim Y. et al. Highly efficient epitaxial Ge solar cells grown on GaAs (001) substrates by MOCVD using isobutylgermane. *Solar Energy Materials and Solar Cells*. – 2017. – Vol. 166. – P. 127-131.

[15] A. Sh.Razzokov. Obtaining GaAs - $Ge_{1-x}Sn_x$ heterostructures from tin solution-melt. *International students and young scientists conference in theoretical and experimental physics*. Lviv, Ukraine. – 2022. – A8.

[16] Saidov A.S. Liquid epitaxy of compensated layers of gallium arsenide and solid solutions based on it. – 1986., – pp. 16-20.

[17] V. M.Andreev, L.M.Dolginov, D.N.Tretyakov. Liquid epitaxy in semiconductor device technology. M. *Soviet Radio Publishing House*. – 1975, –C. 35-44.

[18] Fleurial J. P., Borshchevsky A. Si-Ge-metal ternary phase diagram calculations. *Journal of The Electrochemical Society*. – 1990. – Vol. 137. – №. 9. – P. 2928.

[19] Olesinski R. W., Abbaschian G. J. The Ge− Sn (germanium− tin) system. *Bulletin of Alloy Phase Diagrams*. – 1984. – Т. 5. – №. 3. – С. 265-271.

[20] A. Sh.Razzokov. et al. Features of growing Si-and $Si_{1-x}Ge_x$ -single-crystal films from solution-melt based on tin. *Journal of Physical Studies*. – 2022. – Vol. 26. – №. 4. – P. 4601-1-4601-5. (Scopus IF= 0.131).