ISSN1027-5495. Functional Materials, 32, No.1 (2025), p. 28-34
doi:http://dx.doi.org/10.15407/fm32.01.28 © 2025 — STC "Institute for Single Crystals"

Growing $Ge_{1-x}Sn_x$ solid solutions on Ge, GaAs substrates

A.Sh.Razzokov[1], M.A.Shonazarova[2], J.A.Razzakov[1]

[1] Urgench State University, 14 Kh.Alimdjan, Urgench, 220100, Uzbekistan
[2] Leipzig University, 10 Augustplatz, Leipzig 04109, Germany

Received July 22, 2024

Single-crystal films of the $Ge_{1-x}Sn_x$ solid solution were grown in the temperature range of 893-723 K at a cooling rate of 0.5-1.5 K/min from a limited tin solution-melt. The substrates were Ge(111) and GaAs(100) with a carrier concentration of $n=(1\div5)\cdot10^{17}cm^{-3}$, $n=(4\div7)\cdot10^{17}cm^{-3}$, respectively. The gap between the substrates was 0.65÷1.2 mm. The technological conditions for obtaining a GaAs- $Ge_{1-x}Sn_x$ heterostructure with a smooth substrate-film boundary were achieved, while the supercooling temperature was 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 diffractometry. The film photosensitivity covers the spectral region of 0.5-1.9 eV.

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

Вирощування твердих розчинів $Ge_{1-x}Sn_x$ на підкладках Ge, GaAs. *А.Ш.Раззоков, М.А.Шоназарова, Я.А.Раззаков*

Монокристалічні плівки твердого розчину $Ge_{1-x}Sn_x$ вирощували в інтервалі температур 893-723 К при швидкості охолодження 0,5-1,5 К/хв з обмеженого розчину-розплаву олова. Підкладками були Ge(111) та GaAs(100) з концентрацією носіїв $n=(1\div5)\cdot10^{17}см^{-3}$, $n=(4\div7)\cdot10^{17}см^{-3}$ відповідно. Зазор між підкладками становив 0,65÷1,2 мм. Досягнуті технологічні умови для отримання гетероструктури GaAs-$Ge_{1-x}Sn_x$ з гладкою межею підкладка-плівка, температура переохолодження Т=6,2 °С. Методом рентгенівської дифрактометрії визначено монокристалічність плівки $Ge_{1-x}Sn_x$ ($0 \le x \le 0,03$). Світлочутливість плівки охоплює спектральну область 0,5-1,9 еВ.

1. Introduction

Growing 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 urgent tasks of instrumentation [1, 2].

One of such materials is the $Ge_{1-x}Sn_x$ solid solutions covering the spectral range of Ge and less. $Ge_{1-x}Sn_x$ semiconductor alloys are attractive for use in mid-infrared photodetectors due to their narrow band gap. Therefore, $Ge_{1-x}Sn_x$ is promising for the manufacture of photodetectors and laser devices of the near and mid-infrared range [3, 4]. In [5], the low-temperature molecular beam epitaxy method was used to grow $Ge_{1-x}Sn_x$ films on Ge/AlAs/Al_2O_3 substrates. However, XRD studies show that the grown samples have tetragonal deformation. The presence of twins was more pronounced for the sample grown with a higher chemical Sn content (5.2%), compared to the sample grown with 3.6% Sn. By growing a significantly thicker layer, it was possible to suppress the presence of defects in the epitaxial layers.

InP(001) substrates were used to obtain crystalline perfect $Ge_{1-x}Sn_x$ layers. It was possible to grow $Ge_{1-x}Sn_x$ by low-temperature molecular beam epitaxy at growth tempera-

tures of 70 and 100 °C with a composition of $x \sim 0.25$. 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 analyses showed that $Ge_{1-x}Sn_x$ with a low tin content is formed as a result of tin agglomeration with the formation of In-Sn alloys [6].

The authors of [7] presented the growth of Ge and GeSn at temperatures of 500–600 °C on GaAs (001) substrates using two different buffer layers consisting of Ge/GaAs and Ge/AlAs by molecular beam epitaxy. The quality of Ge layers was studied using X-ray diffraction, atomic force microscopy, and photoluminescence. Using a Ge buffer layer, the direct transition was shifted after the indirect transition to a longer-wavelength region, which allowed the authors to assume the presence of a GeSn material with a direct band gap.

Also, 100 nm thick $Ge_{1-x}Sn_x$ films were obtained by magnetron sputtering in the temperature range of 220–330 K. The films in the range of $0.09 \le x \le 0.15$ had high values of the Seebeck coefficient (α) and power factor. However, the low electrical conductivity of the films complicates their application in the field of thermoelectricity. Nevertheless, using doping, $Ge_{1-x}Sn_x$ is interesting for complementary metal oxide semiconductors [8].

In order to develop high-performance short-wave 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. The XRD, TEM, AFM, and Raman analyses showed that the GeSn/Ge structure reains coherent deformation at 400 °C and the sa mple sensitivity 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] doped Ge (with an indirect band gap) with the semimetal Sn (E = -0.41 eV). Si substrates with a Ge buffer were used as templates for the epitaxy of GeSn layers and softened the mismatch of the lattice parameters of GeSn and Ge, Si (a_{Sn} = 0.6489, a_{Ge} = 0.5658 nm and a_{Si} = 0.5431 nm). First, Ge with a thickness of ~0.1 μm was "seeded" 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 resulted in the formation of threading dislocations.

The possibility of growing crystalline perfect epitaxial layers of solid solutions $(Sn_2)_{1-x}(InSb)_x$ ($0<x<0.95$) from the liquid phase on gallium arsenide substrates with a narrow band gap E_g = 0.11 ÷ 0.12 eV in the temperature range of 598÷533 K was also demonstrated [11, 12]. The main difficulty in obtaining high-quality structures of this 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 had a negative effect on the electrophysical and photoelectric properties. Therefore, the possibilities of synthesizing highly perfect semiconductor solid solutions based on the most studied narrow-band materials are of particular interest.

Taking into account the similar values of the lattice parameters of the GaAs and Ge (a_{GaAs}= 0.5654 nm, a_{Ge}= 0.5658 nm), as well as the similar values of their thermal expansion coefficients $\alpha_{GaAs}=5.93 \cdot 10^{-6}$ K^{-1}; $\alpha_{Ge} = 6.1 \cdot 10^{-6}$ K^{-1}), of great interest is the production of GaAs-$Ge_{1-x}Sn_x$ heterostructures ($0< x < 0.03$), since these 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 lattice parameters and thermal expansion coefficient of the epitaxial layers, but leads to a shift in the photosensitivity of the film to the IR region [15,16].

From the above, there are many theoretical and experimental works in the literature on obtaining crystalline perfect $Ge_{1-x}Sn_x$ solid solutions, and significantly successful results have been obtained. However, obtaining a $Ge_{1-x}Sn_x$ single crystal with high tin content ($x > 0.01$) is difficult due to the insufficient amount of tin included in the solid solution and the growth of epitaxial layers oriented along the substrate direction.

In this work, the technological conditions and physical features for obtaining $Ge_{1-x}Sn_x$ ($0<x< 0.03$) solid solutions and GaAs-$Ge_{1-x}Sn_x$, Ge-$Ge_{1-x}Sn_x$ structures based on them from the liquid phase are presented. The chemical content and single crystallinity of the grown layers and some of their electrophysical photoelectric properties were experimentally determined.

The possibility of growing $Ge_{1-x}Sn_x$ epitaxial layers on a GaAs substrate with smooth substrate-to-film boundaries using supercooling of the solution-melt is shown.

2. Experimental

Epitaxial $Ge_{1-x}Sn_x$ ($0<x<0.03$) films were grown using a vertical-type quartz reactor with horizontally positioned substrates. To prevent uncontrolled impurities from entering the reactor from the atmosphere, the process of growing epitaxial layers was carried out in a hydrogen atmosphere.

The composition of the Ge-Sn melt solution was determined from the phase diagrams of binary Sn–Ge alloys. Literature data [17–19] were used to prepare the liquid melt solution.

Chemically pure (99.999%) Ge(111) and GaAs(100) wafers with charge carrier concentrations of $n = (1\div5)\cdot10^{17}$cm^{-3}, $n = (4\div7)\cdot10^{17}$cm^{-3}, respectively, with donor conductivity type were used as substrates. The diameter of the Ge and GaAs substrates was 50 mm, the thickness was 350-400 μm.

To obtain a specific 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)). The structure and phase composition were studied on high-resolution diffractometers D2 PHASER/Bruker (GID and GONIO modes using HR-XRD, Panalytical/Empyrean).

Electrical resistivity, mobility and concentration of the majority charge carriers were determined using the HMS-5500 (Hall effect measurement system) setup. Spectral characteristics of the samples were measured using a monochromator with a slit diameter of 0.2 mm.

3. Results and Discussion

Based on the above, epitaxial layers $Ge_{1-x}Sn_x$ ($0 < x < 0.03$) were grown from a tin solution-melt in a temperature range of 893-723 K at a cooling rate of 0.5-2 K/min. The composition of the Sn+Ge melt solution and the corresponding growth temperature range corresponded to those described in [20, 21].

The composition of the $Ge_{1-x}Sn_x$ solid solution and the distribution of components in the grown epitaxial layers were studied and presented in Fig. 1.

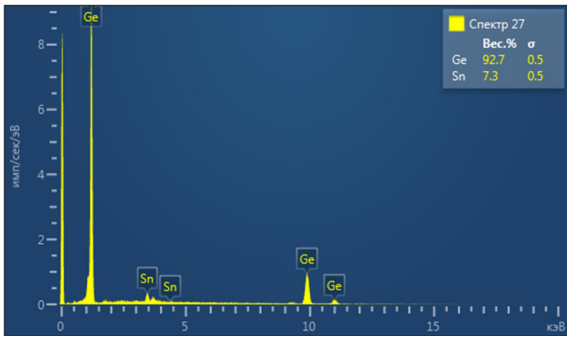

Fig.1. EDS spectrum of the surface of $Ge_{1-x}Sn_x$ epitaxial layers

Crystalline perfect, mirror-smooth layers of the $Ge_{1-x}Sn_x$ solid solution were obtained at the most optimal cooling rate of the solution-melt of 0.5–1.0 K/min. This mode corresponded to the actual crystallization rate of the epitaxial layers of 0.13-0.2 μm/min. The structural perfection of the grown layers also depended on the size δ of the gap between the horizontally located substrates. The most structurally perfect layers of solid solutions on both the upper and lower substrates were grown at δ in the range of 0.65 ÷ 1.2 mm. At δ > 1.2 mm, the quality of the layers grown on the lower and upper substrates differed significantly: layers grown on the lower substrates were always more perfect than those on the upper ones. [22, 23].

Epitaxial films $Ge_{1-x}Sn_x$ were grown from a Ge+Sn melt solution on a Ge substrate. If the melt solution is saturated with the Ge component, a smooth substrate-film boundary structure can be obtained. In this case, thermodynamic equilibrium prevents the melting of the surface layer of the substrate-film interface at the crystallization front [18, 24]. Therefore, using the temperature diagram of the states for the Ge + Sn melt solution system, it was possible to obtain crystalline perfect epitaxial layers without included microtwins and a second phase with defects (Fig. 2).

In the case of a "foreign" GaAs substrate, the unsaturation of the Ge + Sn solution-melt system relative to GaAs will lead to the partial dissolution of the substrate [25]. When growing structurally perfect pure epitaxial layers, this partial dissolution of the substrate is extremely undesirable. To prevent this, it is necessary to achieve an equilibrium state of the system between the liquid (solution-melt) and solid phases (substrate). The liquid phase should be supercooled relative to the solid phase-substrate. Nevertheless, when growing epitaxial layers from a cooled solution-melt, it is also necessary

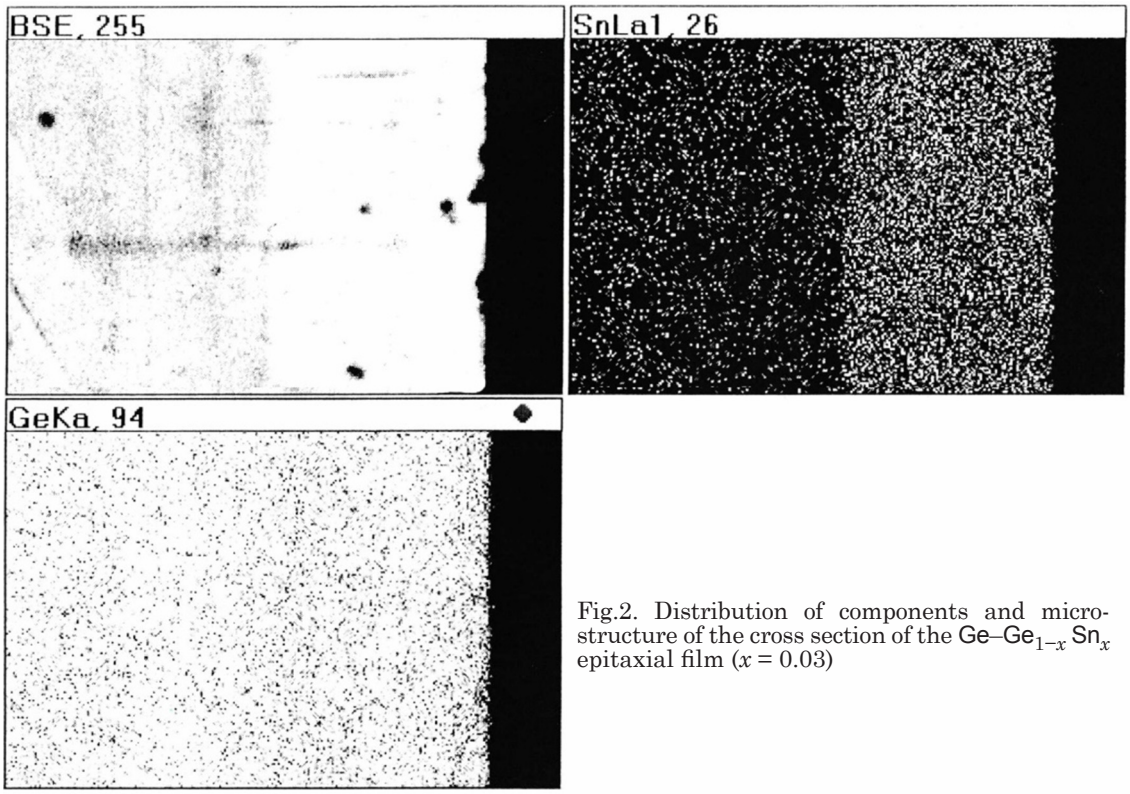

Fig.2. Distribution of components and microstructure of the cross section of the Ge–Ge_{1-x} Sn_x epitaxial film (x = 0.03)

to control the supersaturation value so that too many nuclei do not form, leading to the formation of a polycrystal. Therefore, for the thermodynamic equilibrium of this system, the contact supercooling temperature was determined using the following formula [17, 26]:

$$\Delta T = \frac{T_L}{\Delta H} \cdot \frac{EM}{1-\nu}\left(\frac{a_1 - a_2}{a_1}\right)^2 \cdot \frac{1}{f}$$

where T_L is the liquidus temperature; E is Young's modulus; v is Poisson's ratio; ΔH is the enthalpy of dissolution of the skin layer; M is the molar volume; a_1,a_2 are the lattice parameters of the substrate and the solid phase; f is the stabilization factor.

Based on theoretical calculations, the supercooling temperature (ΔT = 6.2 °C) for the Ge + Sn system melt solution was determined in advance and applied in the growth process. It was found that this supercooling temperature is optimal for growing a $Ge_{1-x}Sn_x$ solid solution on a GaAs substrate from the liquid phase. Thus, the technological condition for obtaining a GaAs- $Ge_{1-x}Sn_x$ heterostructure with crystalline perfection and a smooth substrate-film boundary was achieved (Fig. 3).

A qualitative assessment showed a practically uniform distribution of solution-forming components across the thickness of Ge–$Ge_{1-x}Sn_x$ and GaAs–$Ge_{1-x}Sn_x$ epitaxial films (Fig. 2, 3).

Analysis of raster images and morphological studies of $Ge_{1-x}Sn_x$ solid solutions have shown 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 the main reason for the deterioration of the structure of the epitaxial layers. Relaxation of the resulting significant coherent stresses leads to the formation of dislocations [27, 28]. This difference decreases with the growth of subsequent epitaxial layers, 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 [29]. As a result, a heteroboundary is formed, the thickness and perfection of which can be controlled by changing the growth modes. It was found that with an increase in the tin content in the $Ge_{1-x}Sn_x$ solid solution, the structural perfection of the layers deteriorates sharply and even second-phase precipitates appear.

The crystalline perfection and the change in the lattice parameters of the solid solution

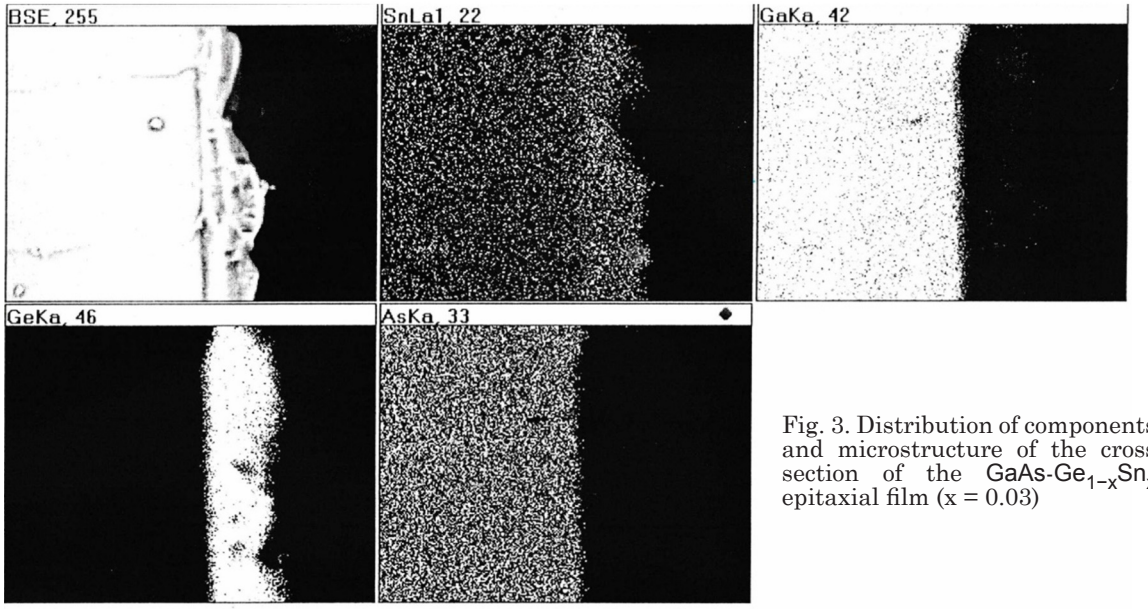

Fig. 3. Distribution of components and microstructure of the cross section of the GaAs-$Ge_{1-x}Sn_x$ epitaxial film (x = 0.03)

were studied by the XRD method (Fig. 4a). The precisely measured lattice parameters of the substrate and the grown film differed insignificantly (a_{Ge} = 0.5656 nm, $a_{Ge1-xSnx}$ = 0.5681nm), and the absence of other diffraction maxima indicated the single-crystal nature of the obtained epitaxial layers.

The surface morphology of the solid solution film was studied using chemical etching to identify defects and dislocations. A mixture of hydrofluoric (HF), nitric (HNO_3) and acetic (CH_3COON) acids in the ratios of 1hHF + 11hHNO_3 + 2hCH_3COOH was used as an etchant. The direction and density of dislocations in the film were determined.

It is evident from Figure 4b that the geometric shape of the dislocations is triangular and they are all directed at the same angle in the same direction. This indicates the single crystallinity of this layer with the orientation <111>.

It has been experimentally established that the dislocation density N_D in the grown semiconductor solid solutions $Ge_{1-x}Sn_x$ depends on the growth temperature of the solid solution. To reduce the dislocation density, the experiments were carried out at different crystallization onset temperatures T_{OC}. The lowest values of the dislocation density (N_D=2·10^4÷8·10^4 cm^{-2}) were recorded in epitaxial films at T_{OC} = 873 K.

The following electrophysical properties of the obtained films were determined: electrical resistivity ρ = (3÷7)·10^{-2} Ohm·cm, Hall mobility μ_p = 50÷110 cm^2/V·s, and concentration of charge carriers at a temperature of 300 K

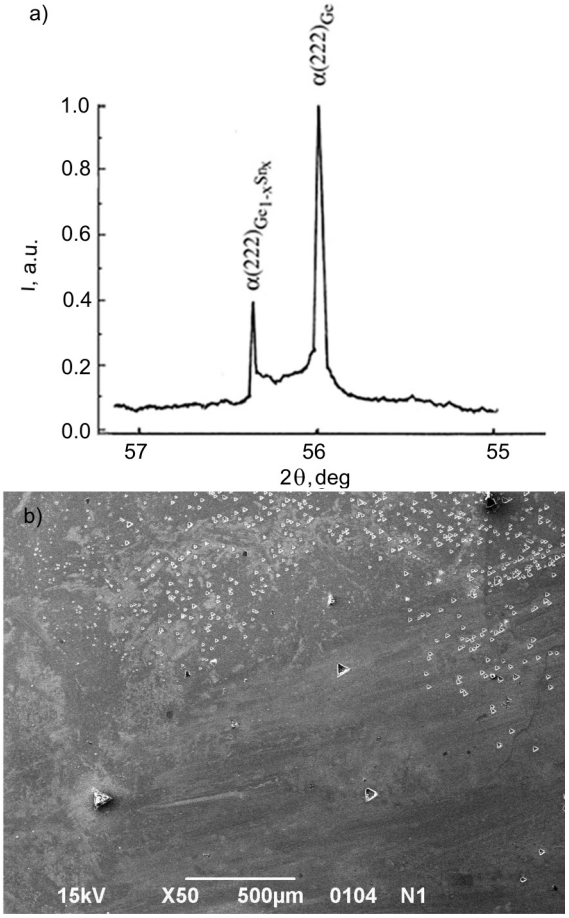

Fig. 4a. Diffraction maxima (222) from (Ge) lattices and the Ge-$Ge_{1-x}Sn_x$ solid solution (x = 0.03); 4.b. SEM image of dislocations on the surface of grown $Ge_{1-x}Sn_x$ epitaxial layers

n_n= (5÷7)·10^{18} cm^{-3}. The films had a hole type

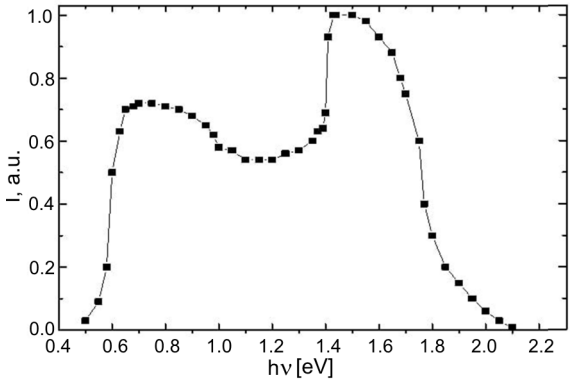

Fig. 5. Photosensitivity of the n$GaAs$-p$Ge_{1-x}Sn_x$ structure in the photodiode mode at a temperature of 300 K

of conductivity.

Gold ohmic contacts were deposited on the $Ge_{1-x}Sn_x$ epitaxial layers and n$GaAs$-$Ge_{1-x}Sn_x$ structures by vacuum deposition, and their photoelectric properties were measured. The photosensitivity of the n$GaAs$-p$Ge_{1-x}Sn_x$ structure was measured in the photodiode mode, illuminating the samples from the film side at a temperature of 300 K (Fig. 5).

The photosensitivity of the heterostructures covered a fairly wide spectral region: 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 the n$GaAs$-p$Ge_{1-x}Sn_x$ structures. Short-wave quanta are partially absorbed in the upper layers of the film. Photons that have passed through the outer layers of the solid solution are absorbed already in the contact region, reaching the p-n junction of the n$GaAs$-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, when the heterostructure is illuminated from the film side, photon energy tunneling occurs. The penetration of photons through a thin (d = 4÷6 μm) $Ge_{1-x}Sn_x$ epitaxial layer onto the n$GaAs$-p$Ge_{1-x}Sn_x$ (substrate-film) heterojunction region creates a photoEMF in the infrared region of the spectrum.

4. Conclusion

Thus, the possibility of growing crystal-perfect epitaxial layers of $Ge_{1-x}Sn_x$ ($0 \le x \le 0.03$) solid solutions on $GaAs$ (100) and Ge (111) substrates by selecting appropriate growth conditions from a limited tin melt solution has been demonstrated. Based on theoretical calculations, the supercooling temperature for the Ge + Sn melt solution determined in advance was ΔT= 6.2 °C. The technological conditions for obtaining $GaAs$-$Ge_{1-x}Sn_x$ heterostructures from the Sn-Ge solution-melt system without sub-dissolution of the "foreign" substrate using supercooling were experimentally established. The photosensitivity of the heterostructures covered a fairly wide spectral range: 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. *Applied Surface Science*, **657**, 159707 (2024). 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. *Materials Science in Semiconductor Processing*. **70**, 139 (2017). 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. *Materials Science in Semiconductor Processing*. **88,** 28 (2018). 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. *Scientific Reports,* **7**, 16114 (2017). https://doi.org/10.1038/s41598-017-16356-8.
5. D.Gayakwad, D.Singh, R.Kumar, Y.I.Mazur Sh.Q.Yu, G.J.Salamo, S.Mahapatra, K.R.Khiangte. *Journal of Crystal Growth,* **618**, 127306 (2023). https://doi.org/10.1016/j.jcrysgro.2023.127306.
6. Sh.Shibayama, K.Takagi, M.Sakashita, M.Kurosawa, O.Nakatsuka. *Materials Science in Semiconductor Processing*. **176**, 108302 (2024). 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, *RSC Advances*, **14**(2), 1250 (2024). https://doi.org/10.1039/d3ra06774b.

8. A. Portavoce, H.Khelidj, N.Oueldna, S.Amhil, M.Bertoglio, D.Mangelinck, L. Essaleh, K. Hoummada. *Materialia,***14**,100873 (2020). 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. *Vacuum*, **210**, 111868 (2023). https://doi.org/10.1016/j.vacuum.2023.111868.
10. J.M. Hartmann, T. Marion. *Materials Science in Semiconductor Processing*, **169**, 107893 (2024). https://doi.org/10.1016/j.mssp.2023.107893.
11. A.S.Saidov, A.Sh.Razzokov, D.V.Saparov. *Letters to the Technical Physics,* **28**(22), 7 (2002).
12. A.Sh.Razzokov, U.P.Asatova, Sh.K. Ismoilov. *Proceedings of the Republican scientific and technical conference with the participation of foreign scientists "Composite materials: Structure, properties and application*". Tashkent, P.136 (2008).
13. H.Liu, Y.Jin. *Procedia engineering*, **215**, 17 (2017).
14. Kim Y. et al. *Solar Energy Materials and Solar Cells*, **166,**127 (2017).
15. A.Sh. Razzokov. *International students and young scientists' conference in theoretical and experimental physics,* Lviv, Ukraine. A8 (2022).
16. Y.V.Znamenshchykov, V.V.Kosyak, A.S.Opanasyuk, M.M.Kolesnyk, V.V.Grinenko, P.M.Fochuk. *Functional Materials*, **23**(1), 32 (2016).
17. A.S. Saidov, M.S. Saidov, E.A. Koshchanov. Liquid epitaxy of compensated layers of gallium arsenide and solid solutions based on it. (Fan, Tashkent) 1986, P. 16-20.
18. V.M.Andreev, L.M.Dolginov, D.N.Tretyakov. Liquid epitaxy in semiconductor device technology. M, Soviet Radio Publishing House. 1975, C. 35-44.
19. J. P.Fleurial, A.Borshchevsky. *Journal of the Electrochemical Society*. **137**(9), 2928 (1990).
20. R. W. Olesinski, G. J. Abbaschian. *Bulletin of Alloy Phase Diagrams*, **5**(3), 265 (1984).
21. A.Sh. Razzokov, A.S.Saidov, S.I.Petrushenko, S.V.Dukarov *Functional Materials*. **29**(2), 202 (2022).
22. A.Sh. Razzokov. et al. *Journal of Physical Studies*. **26**(4), 4601-1 (2022).
23. A.Sh.Razzokov. *Functional Materials*. **30**(2),156 (2023).
24. A. Sh. Razzokov et al. *Journal of Crystal Growth*. **612,** 127203 (2023).
25. M.Ilegems, M.B. Panish. *Journal Phys.Chem. Sol*. **35** 409 (1974).
26. J.W Gibbs. Thermodynamic works. – M. – L.: Gostekhizdat, 1950.
27. Ye.V.Ftomov, O.V.Shekhovtsov, E.E.Badiyan, A.G.Tonkopryad. *Functional Materials*. **28**(4), 652 (2021).
28. O.M.Suprun, G.D.Il'nitskaya, V.A.Kalenchuk, O.A.Zanevskii, S.N.Shevchuk, V.V.Lysakovskii. *Functional Materials*. **23**(4), 552 (2016).
29. A.S.Saidov, A.Sh. Razzokov. *Crystallography Reports*. **67**(2), 301(2022).