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Obtaining semiconductor structures Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ from the liquid phase in a single technological cycle

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By the method of liquid-phase epitaxy in a single technological cycle,semiconductor Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ structures were obtained from a confined tin solution-melt on Si <111> substrates in the temperature range 1100°C–500°C. Some electro-physical and photoelectric parameters of the grown $Si_{1-x-y}Ge_xSn_y$ films were also studied. The microstructural, electrophysical, and photoelectric properties of $Si_{1-x-y}Ge_xSn_y$ films have been investigated,and it was shown that the samples obtained by liquid-phase epitaxy have unique technological characteristics.
Keywords: crystallization, epitaxy, films, solid solution.

Отримання напівпровідникових структур Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ з рідкої фази за один технологічний цикл. *А.Ш.Раззоков, А.С.Саїдов, С.І.Петрушенко, С.В.Дукаров*
Метод рідкофазної епітаксії в єдиному технологічному циклі використано для формування функціональних напівпровідникових Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ плівкових структур. Зразки отримували з обмеженого олов'яного розчину-розплаву на підкладках Si <111> у температурному інтервалі 1100°C–500°C. Досліджено мікроструктурні, електрофізичні та фотоелектричні властивості плівок $Si_{1-x-y}Ge_xSn_y$ і показано, що зразки, які створено з використанням методу рідкофазної епітаксії, мають унікальні технологічні характеристики.

1. Introduction

Growing semiconductor solid solutions based on the elements Si, Ge, Sn of group IV of the Periodic Table is of great practical importance due to the need to create semiconductor structures operating in the infrared spectrum, which can be obtained in a single technological cycle on cheaper substrates, for example, silicon. The formation of ternary SiGeSn compounds and the production of device structures based on them are widely studied in experimental works [1–3]. But the difference between the lattice parameters and thermal expansion coefficients of discrete structures ($a_{Si} = 5.4307 \cdot 10^{-10}$ m, $a_{Ge} = 5.66 \cdot 10^{-10}$ m, $a_{Si} = 5.1 \cdot 10^{-6}$ K^{-1}, $a_{Ge} = 6.1 \cdot 10^{-6}$ K^{-1} etc.) does not allow obtaining crystalline perfect heterostructures. In turn, it is crystallographic perfection that is a necessary condition for the creation of technological structures with high operational characteristics [4, 5]. The epitaxial methods used in [6, 7] are technologically complex and poorly suited for industrial applications.

At the same time, the method of liquid epitaxy from a confined solution-melt is technologically simple and allows one to obtain functional structures on an industrial scale. In contrast to [3, 7, 8], liquid-phase epitaxy makes it possible to obtain variable (with a controlled band gap) epitaxial layers with variable compositions of films along the growth direction, starting from the substrate-film boundary (the beginning of growth) and ending on the surface (the termination of growth) solid solution. Accordingly, this technology makes it possible to smooth out the difference in lattice parameters and thermal expansion coefficients between films and substrates. Due to this,one can expect the crystal perfection of the obtained structures [9, 10].

In this work, single-crystal films of a $Si_{1-x-y}Ge_xSn_y$ solid solution of variable composition on Si <111> and $Si–Si_{1-x}Ge_x–Si_{1-x-y}Ge_xSn_y$ substrates were obtained from a confined solution-melt by liquid epitaxy. The effect of the technological conditions of growing $Si_{1-x-y}Ge_xSn_y$ on the functional properties of the obtained thin-film structures $Si–Si_{1-x}Ge_x–Si_{1-x-y}Ge_xSn_y$ has been studied. The optimal growth conditions were determined, and it was shown that the films obtained under these conditions are crystal perfect with the lowest values of the dislocation density (within $9\cdot10^3–10^5$ cm^{-2}) at the substrate-film interface and over the sample thickness.

2. Experimental

To obtain the $Si–Si_{1-x}Ge_x–Si_{1-x-y}Ge_xSn_y$ structures in a single technological growth cycle, we used a vertical-type quartz reactor with horizontally arranged substrates on an EPOS-type setup. The epitaxial layers were grown from a small volume of a tin solution-melt, bounded by two substrates in a hydrogen atmosphere purified using a palladium catalyst. The simultaneous use of two or more (up to 50) substrates not only made it possible to minimize the amount of consumed solution-melt, but also allowed obtaining two or more samples formed in a single technological cycle. After placing the substrate (horizontally) and the components of the solution, the system was evacuated to a residual pressure of 10^{-2} Pa, purified hydrogen was passed through the reactor at a rate of 0.06 L/min for 30 min, and then the heating of the system began (charge of the solution-melt located in a vertical quartz crucible). When the temperature reached the required value, the system switched to the automatic temperature maintenance mode. Within 40–50 min, the solution-melt was homogenized. Then the substrates (having the same temperature as the melt-solution) on a graphite holder were brought into contact with the melt solution and, after filling the gaps between the substrates with the melt solution, they were raised 1 cm above the solution level. The growth of epitaxial layers of the $Si_{1-x-y}Ge_xSn_y$ system with a programmed temperature decrease at a rate in the range of 0.5–3 deg/min was promptly stopped by draining the melt solution from the substrates using a centrifuge (Fig. 1).

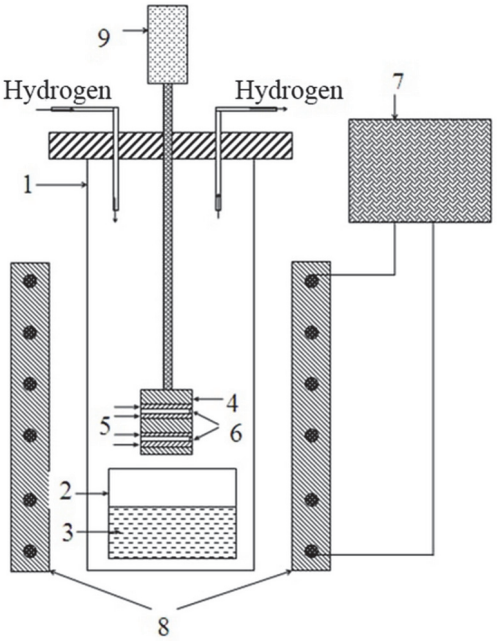

Fig. 1. Schematic diagram of the installation for liquid-phase epitaxy. *1* — quartz reactor, *2* — quartz crucible, *3* — solution-melt, *4* — graphite cassette, *5* — silicon substrates, *6* — graphite supports, *7* — control unit, *8* — thermal block and *9* — electric motor.

The required composition of the solution-melt, consisting of Si, Ge and Sn, was determined on the basis of the phase diagrams of the binary alloys Sn–Si, Sn–Ge. To prepare a liquid solution-melt, the solubility of Si and Ge in Sn was studied in the temperature range of 450–1100°C [13]. Epitaxial films $Si_{1-x-y}Ge_xSn_y$ were grown at the temperature of the beginning (TBC) and the end of crystallization (TEC), respectively, in the range of 1100–500°C.

3. Results and discussion

To study the single crystallinity of the $Si_{1-x-y}Ge_xSn_y$ epitaxial layer grown on the Si (111) substrate, the film growth process

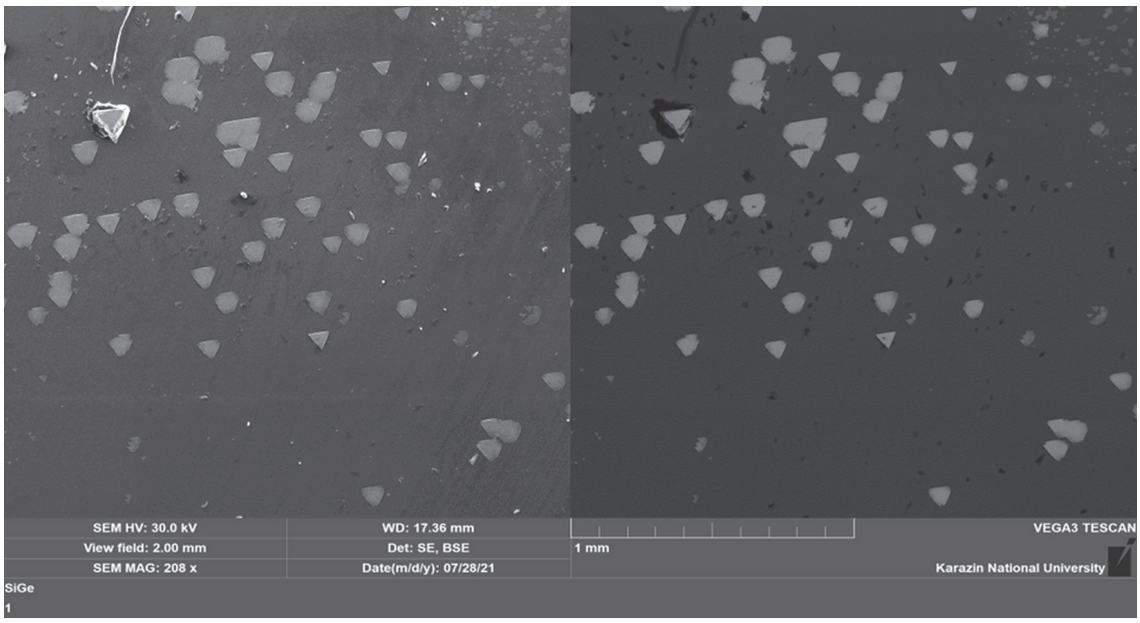

Fig. 2. A snapshot of the beginning of the growth of a $Si_{1-x-y}Ge_xSn_y$ solid solution on a silicon <111> substrate (obtained using a Tescan Vega 3 LMH SEM).

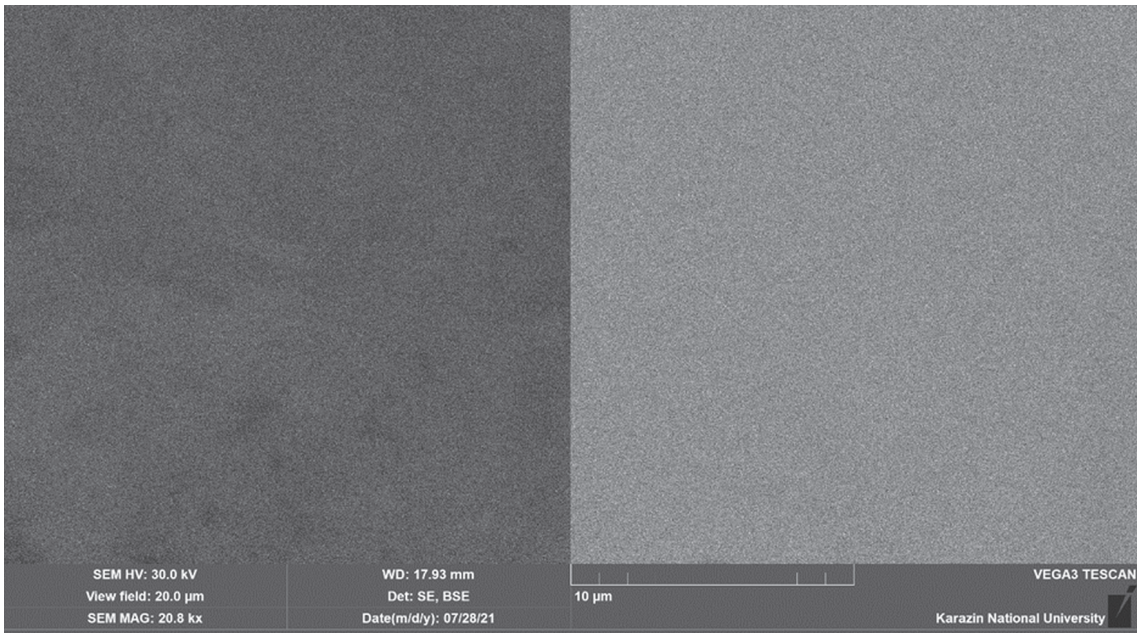

Fig. 3. A snapshot of a specularly smooth surface of the grown $Si_{1-x-y}Ge_xSn_y$ epitaxial layers on a Si <111> substrate (obtained using a Tescan Vega 3 LMH SEM).

was interrupted and the samples were examined using a Tescan Vega 3 LMH scanning electron microscope. At this stage,the SEM images show the surface of nuclei of functional $Si_{1-x-y}Ge_xSn_y$ structures, which are formed along the selected directions of the substrate. The triangles formed at the beginning of growth on the substrate surface show that the epitaxial layers began to grow in the direction of the Si substrate with the (111) orientation (Fig. 2). This allows us to expect that further growth will ensure the formation of single-crystal layers epitaxially continuing the crystal structure of the substrate.

For studying the functional characteristics, the samples were grown at various technological parameters of liquid epitaxy. We grew $Si_{1-x-y}Ge_xSn_y$ epitaxial layers in different temperature ranges (1100°C–500°C) with different qualities of solid solutions (second-phase inclusions, with a rough surface, films with dissolved substrates, etc.). An optimal growth regime has been found that makes it possible to

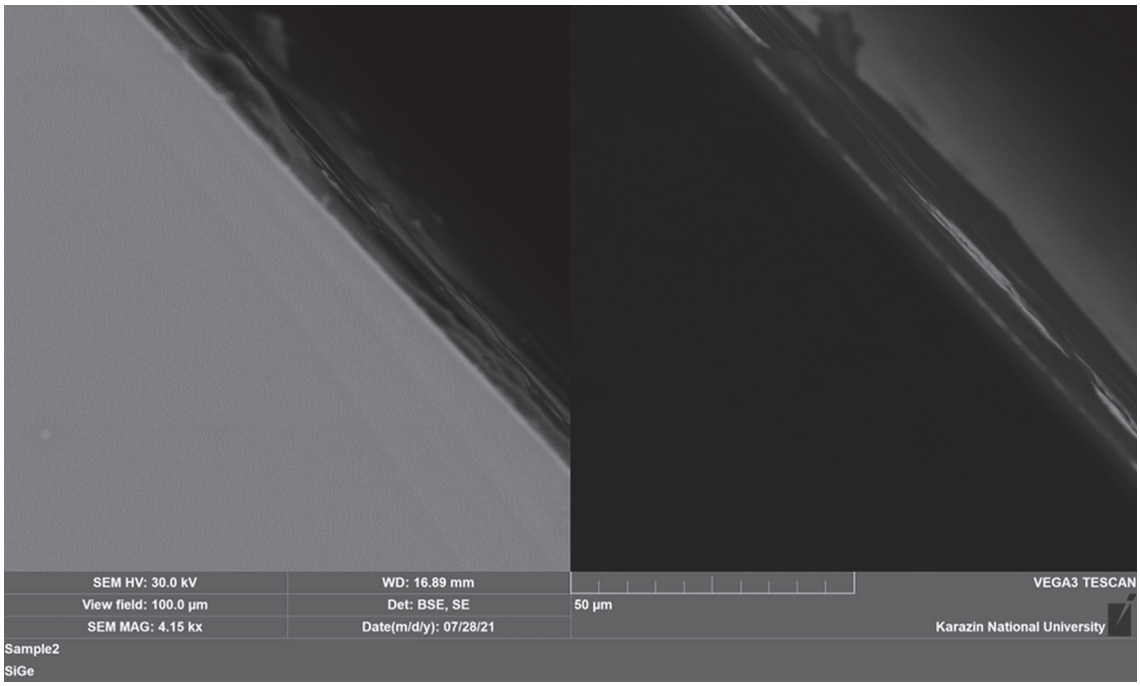

Fig. 4. A snapshot of a cleavage of the Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ structures, obtained using a Tescan Vega 3 LMH scanning electron microscope.

obtain $Si_{1-x-y}Ge_xSn_y$ single-crystal epitaxial layers with mirror-smooth surfaces (namely, TPS and KTP should be in the temperature range of 950–500чС). The surface quality was assessed according to the results of SEM studies (Fig. 3).

The chemical composition of the surface and cleavage of the grown $Si_{1-x-y}Ge_xSn_y$ epitaxial layers were studied using a characteristic X-ray analyzer "Bruker XFlash5010". The resulting raster patterns indicate an almost uniform distribution of the solid solution over the surface of the epitaxial layer and graded in thickness. There are no inclusions of macroscopic defects and the second phase in the film layers (Fig. 4, 5).

The determined chemical composition of the surface of the grown epitaxial films corresponds to the $Si_{0.04}Ge_{0.93}Sn_{0.03}$ solid solution (Fig. 6, Table 1).

It is shown that the growth rate of Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ films also determines the degree of perfection of their crystal structure. When growing epitaxial layers using forced cooling from a solution-melt at a rate (v) of 0.5–1.5 deg/min (TBC and TEC should be in the temperature range of 950–500°C), crystalline perfect solid solutionsare obtained.

With an increase in the cooling rate of the solution-melt above 1.5 deg/min and, accordingly, the growth rate of epitaxial

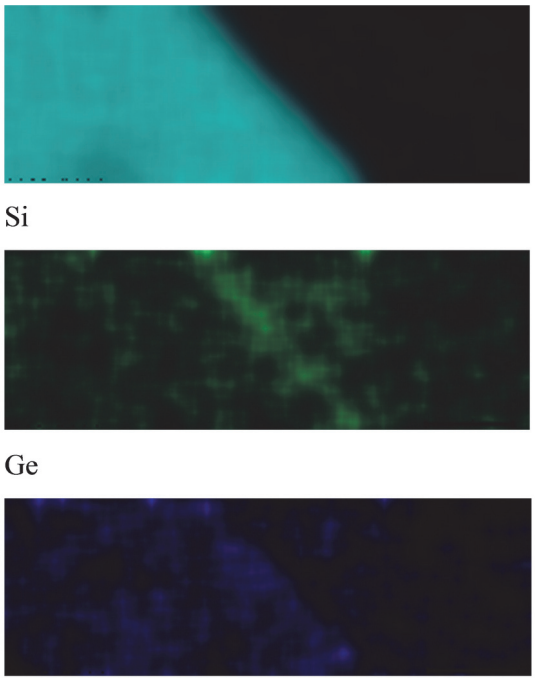

Fig. 5. Elemental maps obtained by cleaving structures Si–$Si_{1-x}Ge_x$–$Si_{1-x-y}Ge_xSn_y$ obtained using a characteristic X-ray analyzer "Bruker XFlash5010".

layers,an uneven growth of films with a rough surface is observed (Fig. 7).

It was found that with an increase in the gap δ between the substrates (i.e., with a change in the volume of the solution-melt

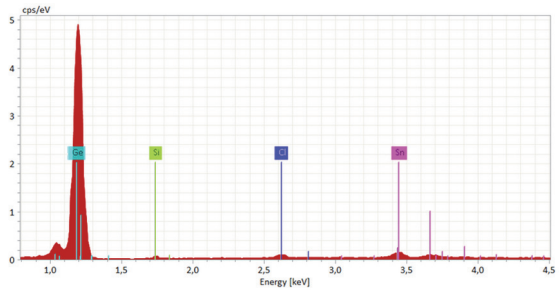

Fig. 6. Quantitative analysis of the surface composition of $Si_{1-x-y}Ge_xSn_y$ epitaxial layers obtained using a scanning electron microscope (when quantifying the EDS spectrum, the "deconvolution only" mode was selected for all impurity elements, mainly sorbed from the atmosphere).

between the substrates), the epitaxial layers grown on the lower and upper substrates do not differ from each other in the degree of crystal perfection of the surface and the substrate-film boundary up to $\delta = 1.4$ mm (with a gap of $\delta < 0.5$ mm, with a high probability, the solution-melt cannot be located between the substrates). At $\delta > 1.4$ mm, the layers on the upper substrates are always thicker and of lower quality than those on the lower ones. This is due to the convection flows of the components in a confined solution. In the literature [14], this is explained by the supply of mass,a convection flow of a solution between horizontally located substrates in a gravitational field. We believe that the field interacts with the force of Archimedes

Table 1

No.	Elements	Atomic, %
1	Germanium	93.4
2	TiN	3.04
3	Silicon	3.56
	Sum:	100

and gravitation, as well as the convection flow; therefore, with a high concentration, Si and Ge accumulate more near the surface of the upper substrate than on the lower one, which accelerates the growth rate of epitaxial layers $Si_{1-x-y}Ge_xSn_y$, and worsens the crystalline perfection of the grown epitaxial layers.

We also studied some of the electrophysical parameters of the grown $Si_{1-x-y}Ge_xSn_y$ epitaxial layers. From the Hall measurements, the resistivity ρ, the concentration of charge carriers n, and the Hall mobility μ of the film were determined. The dislocation density in the layers was determined by chemical etching. The measurements gave the following results: $\rho = 0.5–12$ Ω·cm, $n = 2 \cdot 10^{16}–5 \cdot 10^{17}$ cm^{-3}, $\mu_n = 600–1300$ cm^2/V·s (at a temperature of 300 K) and $N_D \sim 10^5$ cm^{-2} at the substrate-film interface, $N_D \sim 9 \cdot 10^3$ cm^{-2} at the film surface. It can be seen that some of its electrical parameters of the film are close to those for Si, Ge, and $Si_{1-x}Ge_x$ single crystals will make it possible to use $Si–Si_{1-x}Ge_x–Si_{1-x-y}Ge_xSn_y$

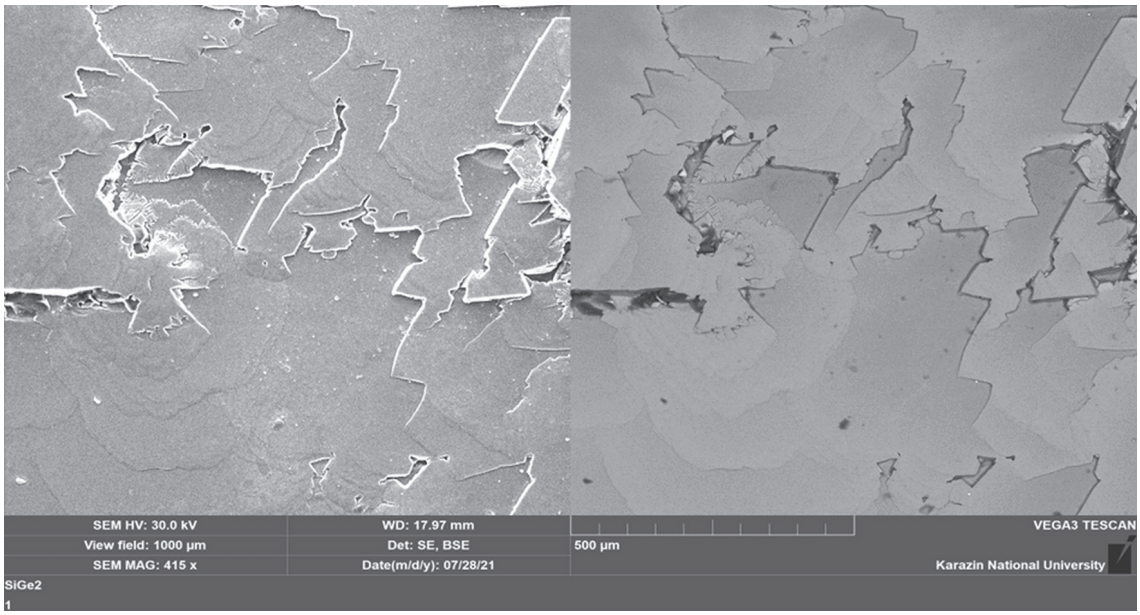

Fig. 7. Surface roughness of $Si–Si_{1-x}Ge_x–Si_{1-x-y}Ge_xSn_y$ structures upon forced cooling of the solution-melt at a rate of $v > 1.5$ deg/min.

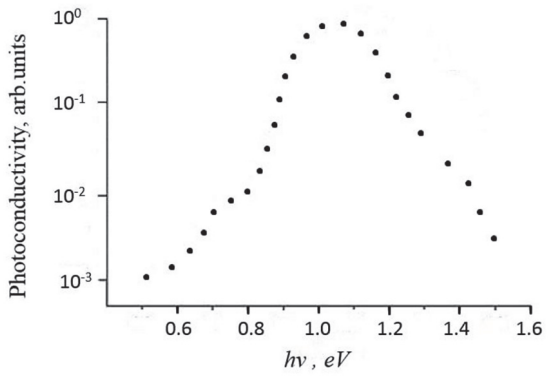

Fig. 8. Photosensitivity of the pSi–nSi$_{1-x}$Ge$_x$–nSi$_{1-x-y}$Ge$_x$Sn$_y$ structure in the photodiode mode at a temperature of 300 K.

structures in semiconductor devices as a material with new electrophysical characteristics obtained on a cheaper Si substrate. Additionally, it is possible to control the electrophysical and photoelectric parameters of the films by changing the growth mode in a certain limited range. The method of liquid-phase epitaxy makes it possible to obtain Si$_{1-x-y}$Ge$_x$Sn$_y$ films and Si–Si$_{1-x}$Ge$_x$–Si$_{1-x-y}$Ge$_x$Sn$_y$ structures with the lowest dislocation densities compared to other discrete heterostructures. The application of the method ensures the crystalline perfection of the samples, and, accordingly, high electrophysical and photoelectric properties.

To study the photoelectric properties of Si$_{1-x-y}$Ge$_x$Sn$_y$ epitaxial layers and pSi–nSi$_{1-x}$Ge$_x$–nSi$_{1-x-y}$Ge$_x$Sn$_y$ structures, gold ohmic contacts were deposited by vacuum deposition. The photosensitivity of the pSi–nSi$_{1-x}$Ge$_x$–nSi$_{1-x-y}$Ge$_x$Sn$_y$ structure was measured in the photodiode mode at a temperature of 300 K (Fig. 8). The photosensitivity was studied using epitaxial films 12–15 μm thick.

The measurement results show that the pSi–nSi$_{1-x}$Ge$_x$–nSi$_{1-x-y}$Ge$_x$Sn$_y$ structures are photosensitive in a fairly wide spectral range: from 0.5 to 1.5 eV. The maximum photosensitivity is observed in the range of 0.95–1.2 eV. The shift in the range of photosensitivity of structures to a longer wavelength region (0.5 eV) as compared to single crystals of Si, Ge, Si$_{1-x}$Ge$_x$ and structures based on them is probably due to the presence of Sn in the composition of Si$_{1-x-y}$Ge$_x$Sn$_y$ films, which corresponds to the results other authors [8, 12].

The photosensitivity in the short-wavelength region is explained by the weak absorption of the solid solution in this region. So shortwave quanta are partially absorbed in the upper layers. The photons that have overcome the outer layers of the solid solution, which is characterized by a narrow absorption band, are absorbed by silicon. Therefore, the maximum of the photosensitivity spectrum is observed precisely in the absorption region of Si. The shift of the photosensitivity range to a longer wavelength region in the pSi–nSi$_{1-x}$Ge$_x$–nSi$_{1-x-y}$Ge$_x$Sn$_y$ structures will make it possible to obtain (depending on the technological growth mode) cheaper semiconductor devices operating in the IC range.

4. Conclusions

In this work, we have shown the possibility of obtaining crystalline perfect epitaxial layers Si$_{1-x-y}$Ge$_x$Sn$_y$ and structures Si–Si$_{1-x}$Ge$_x$–Si$_{1-x-y}$Ge$_x$Sn$_y$ using the liquid epitaxy method. The high perfection of functional structures is ensured by smoothing the difference in the lattice parameters of the substrate-film system (due to a smooth change in the chemical composition of the film) along its growth direction. The objects under study are a promising semiconductor material for the creation of IR spectrum devices. The optimal modes for growing crystalline perfect Si1-x-yGex Sny epitaxial layers from a confined tin solution-melt on single-crystal Si substrates with the (111) orientation have been determined. The optimal technological parameters are as follows:

— T_{BC} in the range from T_{BC} = 850°C to T_{EC} = 950°C;

— forced cooling of the solution-melt at a rate of 0.5–1.5 deg/min;

— the gap between the substrates (corresponds to the height of the solution-melt layer) in the range of 0.5–1.4 mm.

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