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INVESTIGATION OF SILICON SAMPLES DOPED WITH TERBIUM AND THULIUM

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Abstract
This paper presents experimental results of the effect of thulium and terbium impurities on electrophysical parameters, as well as their interaction with background impurities of single-crystal silicon grown by the Czochralski method, doped by diffusion at a temperature of 1250°C for 50 hours followed by rapid cooling. The results of estimating the concentration of optically active oxygen and carbon using an IR Fourier spectrometer are presented, the value of which decreased to 40% for oxygen and to 35% for carbon, respectively, after high-temperature diffusion annealing and rapid cooling.

Keywords: monocrystalline silicon, rare earth elements, thulium, terbium, alloying, diffusion method, thermosonde, four-probe, Van der Pau method, infrared Fourier spectrometer FSM-2201.

Introduction
Alloying single crystals of silicon with rare earth elements has a wide range of applications in various technological fields and remains an urgent area of research aimed at improving the properties of materials and creating new technological solutions. This includes improving the properties of semiconductors, light and magnetic characteristics, solar cells, special optical applications, sensors and detectors.

This paper presents the results of a study of the diffusion process in silicon single crystals grown by the Czochralski method, as well as the effect of the rare earth element terbium on these parameters.

Data on the diffusion of rare earth elements such as terbium (Tb) and thulium (Tm) are limited. Table 1 shows the values of ΔE (eV) — activation energy, D_0 — diffusion coefficient, sources of diffusion data and links to the authors' works.

Table 1

	ΔE, eV	$D_0, sm^2 s^{-1}$	The source of diffusion	Literature
Tb	9,03	$4 \cdot 10^{-1}$	-	[1]
	4,0	$1{,}4 \cdot 10^3$	Tb_2O_3	[8]
	3,3	$5 \cdot 10^{-2}$	$^{160}Tb_2O_3$	[7]
Tm	6,08	-	-	[1]
	3,0	$8 \cdot 10^{-3}$	$TmCl_3$	[11]

Many authors [1, 6] used the method of electrical conductivity, which is indirect, but the reliability of its results remains questionable, since the question of the electrical activity of rare earth elements in silicon doped by diffusion has not yet been resolved. In addition, there is no consensus on the mechanism of diffusion of rare earth elements into silicon. According to the authors [9], the diffusion of ytterbium (Yb) occurs along the path of incorporation with the formation of a solid solution of incorporation. Other researchers [6] claim that lanthanide atoms (Er, Pr, and Tm) diffuse along the nodes of the crystal lattice, similar to other elements of group III of the periodic table. Theoretical and experimental results on the vacancy mechanism of diffusion of the rare earth elements terbium (Tb) and holmium (Ho) with the participation of a chemical reaction are presented in [8].

Theoretical calculations of geometric and electrochemical factors performed in accordance with the method described in [2] show that the probability of formation of a solid solution of substitution is small, while the probability of formation of a solid solution of embedding is much higher.

Based on the above, diffusion of terbium or thulium atoms into n-type monocrystalline silicon samples grown by the Czochralski method was carried out. Before diffusion, the samples were subjected to mechanical and chemical treatment, after which metal layers of Tb or Tm atoms were applied to their surface by vacuum spraying on the VUP-4 installation at a vacuum of 10-3 mmHg. Granules of the corresponding metals with a purity of 99.99% were used as the starting material. High-temperature diffusion annealing was carried out in a horizontal muffle furnace at a temperature of 1250 °C for 50 hours. For rapid cooling after diffusion annealing, ampoules with samples were dipped into transformer oil, the temperature of which was equal to 1-2 ° C. This cooling method is effective for quickly achieving thermodynamic equilibrium of the crystal structure.

The layer-by-layer analysis was carried out using the resistivity measurement method using four probes: one layer of the sample was removed, after which the resistivity was measured. After removing the layer with a thickness of 35-45 microns, the resistivity

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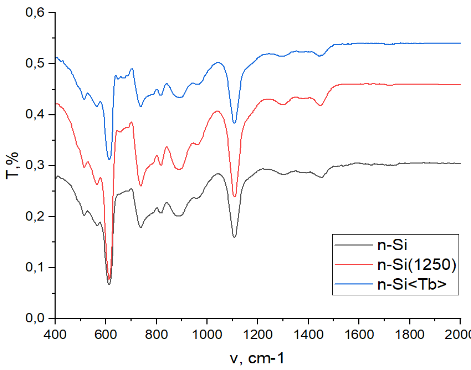
of the alloyed samples approached the value of the control samples. Table 2 shows the values of the main electrophysical parameters of the samples.

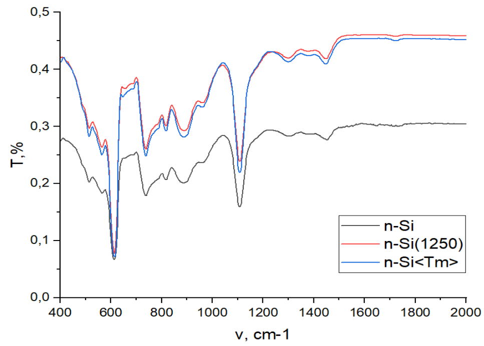
Table 2

№	Sample	ρ, Ohms · cm	$\mu, sn^2/V \cdot s$	n, sm^{-3}
1.	n-Si	30,5	1462	$1{,}4 \cdot 10^{14}$
2.	n-Si (1250 °C)	29,2	500,4	$4{,}27 \cdot 10^{14}$
3.	n-Si<Tb>	19	1192	$2{,}75 \cdot 10^{14}$
4.	n-Si<Tm>	20,2	739	$4{,}2 \cdot 10^{14}$

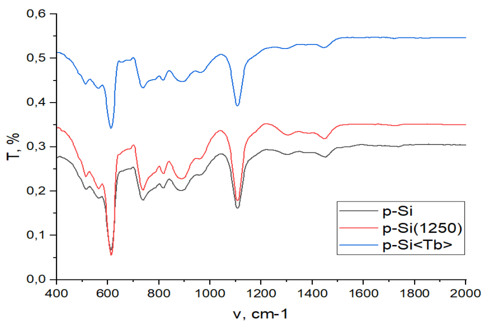
As can be seen from Table 2, the resistivity of the alloyed samples decreased. According to theoretical calculations, the diffusion depth at a temperature of 1250 ° C is 10-15 microns. The type of conductivity of the sample varied in a layer approximately equal to the diffusion depth. However, according to theoretical calculations, the atoms of rare earth elements are electrically inert, so a change in the type of conductivity may be due to the presence of precipitation, silicides and other defects formed during high-temperature processing and rapid cooling.



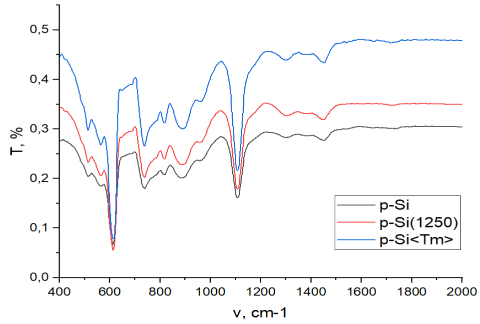
(1-a)



(1-b)



(2-a)



(2-b)

Fig. 1. IR spectra of silicon samples 1 - for n-type (a-for Tb and b-for Tm) and 2 - for p-type (a-for Tb and b-for Tm)

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The authors of [4, 10] argue that the kinetics of thermodonor formation is determined by a number of properties of the initial silicon material, in particular the content of optically active oxygen and carbon, the degree of alloying and the type of impurities in the alloy, as shown in a number of studies [5, 8, 10], where alloying with rare earth elements was used for internal gettering.

The FSM-2201 infrared Fourier spectrometer was used to study changes in the concentration of optically active oxygen and carbon. The results obtained to estimate the concentration of oxygen and carbon are shown in Table 3.

Table 3

№	Sample	N_O, sm^{-3}	N_C, sm^{-3}
1.	n-Si	$6{,}939\cdot 10^{17}$	$0{,}377\cdot 10^{17}$
2.	p-Si	$7{,}702\cdot 10^{17}$	$0{,}103\cdot 10^{17}$
3.	n-Si (1250 °C)	$5{,}990\cdot 10^{17}$	$0{,}519\cdot 10^{17}$
4.	p-Si (1250 °C)	$6{,}472\cdot 10^{17}$	$0{,}200\cdot 10^{17}$
5.	n-Si<Tb>	$2{,}082\cdot 10^{17}$	$0{,}130\cdot 10^{17}$
6.	p-Si<Tb>	$1{,}760\cdot 10^{17}$	$0{,}106\cdot 10^{17}$
7.	n-Si<Tm>	$6{,}315\times 10^{17}$	$0{,}289\times 10^{17}$
8.	p-Si<Tm>	$7{,}209\times 10^{17}$	$0{,}069\times 10^{17}$

As can be seen from Table 3 and Figure 1, the diffusion of rare earth elements into monocrystalline silicon led to a decrease in the content of optically active oxygen and carbon by 40% compared with the initial values. This may indicate that REE actively interact with oxygen and carbon atoms in the crystal structure of the samples.

There are no data on the electrical activity of rare earth elements (REE) in silicon in the modern literature. Moreover, the difference in the radii of covalent bonds between REE and the Si matrix element indicates a low probability of formation of solid substitution solutions, that is, the probability that REE atoms will occupy nodes in the crystal lattice is extremely small. When atoms are replaced in the crystal lattice, the radii of covalent bonds vary greatly, which leads to the formation of point defects around the atoms, causing an increase in elastic deformation.

According to theoretical calculations, the diffusion depth at 1250 °C is 10-15 microns. The type of conductivity of some samples varied in the layers corresponding to the diffusion depth. Theoretical calculations show that a change in the type of conductivity may be associated with the formation of precipitation, silicides and other defects that occur during high-temperature processing and rapid cooling, since the atoms of rare earth elements are electrically inert, but can actively interact with background impurities in the crystal structure of silicon single crystals grown by the Chokhralsky method, as indicated by the results obtained, allows to estimate the concentration of optically active oxygen and carbon.

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