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DOPING A SILICON SINGLE CRYSTAL WITH THULIUM BY THE DIFFUSION METHOD

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Abstract

Using the diffusion method, monocrystalline silicon samples doped with thulium were produced at a temperature of 1,250°C for 50 hours. After high-temperature annealing, it was found that the p-type conductivity of the samples changed to n-type due to the diffusion process.

Keywords: monocrystalline silicon, rare earth elements, thulium, terbium, diffusion method, alloying, hall effect, van der paa method, type of conductivity, concentration of charge carriers, resistivity, scanning electron microscope (SEM).

Introduction

As is known, silicon doped with rare earth elements (REEs) has been attracting increasing attention from researchers as a promising material for optoelectronics. This is due to its potential use in SiREE structures for light sources in silicon-based optoelectronic devices such as SiEr, at a wavelength of 1.54 mm, which corresponds to minimal loss and dispersion in fiber-optic communication systems.

From the perspective of the properties of the electronic shells of this group of elements, there are several advantages. It should be noted that, for silicon, which is the main material in semiconductor microelectronics, REE doping has now been reliably demonstrated to increase the resistance of its key electrophysical parameters against irradiation due to the interaction between REE inclusions and vacancies. It is generally believed that these impurities in silicon are electrically and chemically inert [3-6]. However, their activity may become apparent under certain conditions, such as elevated temperatures.

The authors of a study [3] investigated the effects of impurities from rare-earth elements (REEs) on the kinetics of thermal donor accumulation. They noted that REE atoms interact actively with oxygen in silicon, both during the growth from a melt and during solidification. This results in a sort of "cleaning" of the material.

Currently, there are two opposing views regarding the purification process. One theory is that chemical reactions occur between REEs and background impurities in the liquid phase, leaving the resulting compounds in the slag and not entering the solid phase. Another theory is that REE compounds combine with impurities from nonmetals and enter the growing crystal or epitaxial layer, but these compounds are electrically neutral.

Sample preparation and experimental methods: The study used monocrystalline silicon samples of grades KEF-40 and KDB-20, with crystallographic orientations of {111} and {100}, respectively. The resistivity of these samples was . The samples were mechanically and chemically treated before diffusion, and then a layer of Tm impurity atoms was sprayed onto the surface of the samples using a VUP-4 vacuum apparatus at a pressure of 10 to 3 millimeters of mercury. The source material was granules with a purity of 99.99%. Using an MII-4 microscope, the thickness of the impurity atom layer formed was measured and was found to be 600 nanometers.

As is known, the diffusion coefficient characterizes the rate at which a system returns to its equilibrium position.

$$D = D_0 \exp\left(-\frac{\Delta E}{kT}\right) \quad (cm^2/s) \qquad (1)$$

Based on the theoretical and experimental data from scientific and research papers [7, 8], the temperature dependence of the diffusion coefficient of Tm and Tb impurities in silicon follows an Arrhenius law and can be modeled by the following equations:

$$D_{Tm} = 8 \cdot 10^{-2} \exp\left(-\frac{3.0eV}{kT}\right), cm^2 s^{-1} \qquad (2)$$

Based on the data from [7] and [8] as well as theoretical calculations of the diffusion coefficient and depth, we made a decision about the duration and temperature for the diffusion anneal. The diffusion anneal for the prepared samples was performed in an electric furnace using SOUL-4 branded pumped quartz ampules at a pressure of 10 to 3 millimeters of mercury and a temperature of 1250 degrees Celsius for 50 hours. To quickly cool the samples after the diffusion anneal process, the ampules were immersed in transformer oil at a temperature between 10 and 15 degrees Celsius.To quickly cool, ampules with samples after diffusion annealing were cooled in a transformer oil with a temperature of 1 to 2°C. This method of cooling helps to rapidly bring the crystal structure into thermodynamic equilibrium.

As the concentration of vacancies in the crystal lattice increases at higher temperatures, the likelihood of filling these vacancies with impurity atoms also increases. This approach has been selected based on theoretical calculations.

n-type control samples (10 pieces) and p-type control samples have been examined (10 pieces).

The results of the study of the conduction type of the samples show that the samples with electronic conduction after diffusion annealing do not change their conduction type, while the samples with hole conduction change their conduction type after diffusion to electronic, which raises questions, since, according to literature data, silicon elements are electrically inert.In addition, based on the conditions described in [9], the difference in covalent radii between the substituent element and the host element, silicon, indicates that the environment for forming a solid solution is not favorable.

With each change in the type of surface conductivity, using carborundum powder with grain sizes of 12-14 micrometers, a layer of 10-12 micrometers was removed from the samples using sanding. Measurement results indicated that in samples with hole-type conductivity, when doped with tullium (at 1,250 degrees Celsius for 50 hours), they change to an electronic type of conductivity to a depth of 730 micrometers on both surfaces. Electrophysical properties of the doped samples were measured using van der Paul's method and the results are presented in table 1.

Table 1.

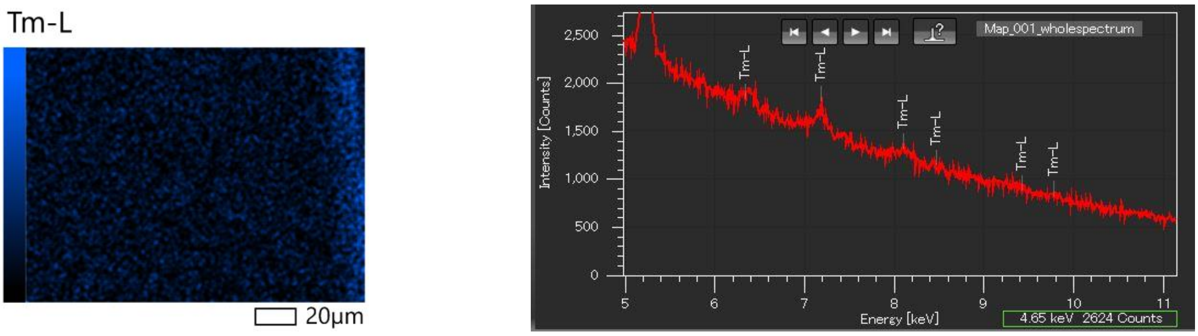
№	Samples	Type	**ρ**, Ohms · cm	**μ**, , $cm^2/V \cdot s$	**n**, cm^{-3}
Initial samples					
1.	n-Si	n	41,1	1406,9	1,07·10^{14}
2.	p-Si	p	20,4	408,7	7,35·10^{14}
Control samples					
1.	n-Si, KEF-40	n	36,3	1063,2	1,6·10^{14}
2.	p-Si, KDB-20	p	16,7	256,2	1,5·10^{15}
Alloyed samples					
1.	n-Si<Tm>	n-n	38,2	1231	1,54·10^{14}
2.	p-Si<Tm>	p→n	14,3	132	3,3·10^{15}

As can be seen in Table 1, the resistivity of the control samples decreased after prolonged heat treatment and after thulium (Tm) doping. The n-Si:Tm samples also decreased in resistivity, and the charge increased.

The surface morphology of the samples was also investigated using a JEOL JSM-IT200 Growth Electron Microscope to identify impurity atoms on the sample surface. Measurement results and SEM spectra are shown in Figure 2.

In order to achieve our goals and optimize the measurements, we sanded the samples from the sides inward, removing 0.3 mm.

After preparation, we fixed the sample substrate with the samples on a microscope stage and placed it in a chamber where we started an air pump process. The accelerating voltage was set to 20 kV, the electron energy to 10 keV, the probe current to 1 pF, and the current intensity to 5 x 10^5.The theoretical depth of electron penetration was calculated using an empirical formula and was found to be 3 nanometers. Figure 1 shows one to two thulium atom clusters on the sample surface, along with a spectrum of intensity as a function of electron energy.



(1) (2)

Fig. 1.

The presence of 1.4-2.2% thulium atoms relative to the mass at the measurement points indicates the need for more accurate measurements using other methods.

Conclusion:

In this work, we have used monocrystalline silicon to dope it with impurity atoms, such as tullium and terbium, using the diffusion method. We have investigated the main electrophysical parameters of the doped material. Using a thermosonde and Van de Pau' method, we determined that the conduction type changes from hole-type to electron-type with terbium diffusing into silicon within a thickness of 30-40 microns. The tullium diffusion depth, on the other hand, is 730 microns.Based on the analysis of experimental and literature data, we have drawn the following conclusions:

- Considering that lanthanides are part of the group of elements on the periodic table, it is possible that REE (rare-earth elements) atoms, due to severe damage to the silicon lattice, may occupy a lattice position, despite their large atomic size. This would result in acceptor properties, although it is not possible to rule out the possibility of forming impurity-defect complexes.
- During diffusion annealing for 50 hours, oxygen-containing centers of electrical activity accumulate in the silicon structure. These centers can affect the electrical properties of silicon.

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