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DOPING A SILICON SINGLE CRYSTAL WITH TERBIUM THROUGH DIFFUSION.

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Abstract: Using the diffusion method, monocrystalline samples of silicon doped with Thulium were prepared at 1250 degrees Celsius for 50 hours. The samples were found to have p-type conductivity after high-temperature annealing. After this process, the samples changed their type of conductivity from p-type to n-type.

Keywords: monocrystalline silicon, rare-earth elements, Terbium, diffusion method, alloying, Hall effect, Van der Pau method, type of conductivity, concentration of charge carriers, resistivity

ЛЕГИРОВАНИЕ МОНОКРИСТАЛЛА КРЕМНИЯ ТЕРБИЕМ ПУТЕМ ДИФФУЗИИ.

Аннотация: Методом диффузии были приготовлены монокристаллические образцы кремния, легированного тулием, при температуре 1250 градусов Цельсия в течение 50 часов. Установлено, что после высокотемпературного отжига образцы обладают проводимостью p-типа. После этого процесса образцы меняли тип проводимости с p-типа на n-тип.

Ключевые слова: монокристаллический кремний, редкоземельные элементы, тербий, диффузионный метод, легирование, эффект Холла, метод Ван дер Пау, тип проводимости, концентрация носителей заряда, удельное сопротивление.

INTRODUCTION

The research into alloying silicon with rare earth (REE) elements is part of a broader investigation into materials science. This could lead to the creation of more efficient and environmentally friendly technologies with improved properties and a wide range of potential applications. The alloying process could be used to develop energy-efficient materials used in LED (light-emitting diode) lamps, which would use less energy and last longer. It should be noted that for silicon, the main constituent material in semiconductor microelectronics, there has been a reliable body of evidence to suggest that REE (rare-earth) doping increases the resistance of a material's electrophysical properties to irradiation due to interactions between REE inclusions and vacancies. It is believed that these impurities are both electrically and chemically inactive in silicon, but their activity may manifest itself under certain conditions, such as elevated temperatures.Currently, there are two opposing opinions regarding the purification process. The first opinion states that chemical reactions between rare earth elements and background impurities take place in the liquid phase, and the resulting compounds are left in the slag and don't enter the solid state. The second view argues that rare earth complex compounds with non-metal impurities enter the growing crystal (or epitaxial layer), but they are electrically neutral. The interest in silicon doped with rare earth elements lies in the potential to create electroluminescent structures on silicon substrates [4]. There is no widespread technology like diffusion for manufacturing silicon structures with REEs. This is due to their low concentration, which results from the low solubility

of rare earths in silicon. However, the concentration of rare earth elements during diffusion depends significantly on the parameters of the diffusion process.It is also possible to achieve a concentration of 3×10^{18} cm^{-3} with diffusion alloying.

SAMPLE PREPARATION AND EXPERIMENTAL METHODS

The study used monocrystalline silicon samples grown by the Czochralski method, which were graded as KEF-40 and KDB-20 with crystallographic orientations of {111} and {100}, respectively. The resistivity of the samples was 1.2 Ωcm. The concentrations of oxygen and carbon in the samples were determined using infrared absorption bands at 9.1 μm and 16.6 μm, respectively.

Before diffusion, the samples were mechanically and chemically treated. A metal layer of terbium (Tb) atoms was then deposited on the surface of the sample using vacuum spraying at a pressure of 10^{-3} mbar using VUP-4. The source material for this process was granules with a purity of 99.99%. To measure the thickness of the resulting impurity atom layer, an MII-4 microinterferometer was used, yielding a value of 520 nanometers. Since rare earth elements can be highly reactive, the prepared samples were then placed inside quartz tubes for diffusion. After the air in the tubes was evacuated, both ends of the tubes were sealed.

Based on the data from references [7] and [8] as well as theoretical calculations of the diffusion coefficients and depths, a decision was made regarding the duration and temperature for diffusion annealing. A diffusion annealing process lasting 50 hours was carried out in a horizontal SOUL-044 muffle furnace at a temperature of 1,250 degrees Celsius.

The temperature of the furnace was monitored using two platinum-rhodium-platinum thermocouples, and the temperature fluctuations were within ±2 degrees Celsius. To quickly cool the samples in ampoules after the diffusion annealing, they were cooled in a transformer oil at a temperature between 1 and 2 degrees Celsius. This method ensures the crystal structure reaches thermodynamic equilibrium quickly.

Due to an increase in vacancy concentration in the crystal lattice at higher temperatures, there is a higher probability that impurity atoms will fill these vacancies.This approach was based on theoretical calculations and selected accordingly. N-type control samples (10 pieces) and p-type control samples were examined (10 pieces). The results of examining the conductivity type of the samples showed that the samples with electronic conductivity did not change their conductivity type after diffusion annealing. However, the samples with hole conductivity changed their conductivity to electronic type after diffusion, which raises questions, since, according to literature data, silicon is electrically inactive. In addition, based on the conditions described in [9], the difference in covalent radii compared to the matrix element (i.e., silicon), indicates that the environment for forming a solid solution is not favorable. The electrophysical parameters of the doped samples were measured using Van der Pau's method, and the results are presented in Table1.

Table 1.

№	Samples	Type	$\boldsymbol{\rho}$, Ohms · cm	$\boldsymbol{\mu}$, , $cm^2/V \cdot s$	$\boldsymbol{n}$, cm^{-3}
	Initial samples				
1.	n-Si	n	41,1	1406,9	$1{,}07 \cdot 10^{14}$
2.	p-Si	p	20,4	408,7	$7{,}35 \cdot 10^{14}$
	Control samples				
1.	n-Si, KEF-40	n	36,3	1063,2	$1{,}6 \cdot 10^{14}$

2.	p-Si, KDB-20	p	16,7	256,2	$1,5\cdot10^{15}$
Alloyed samples					
1.	n-Si<Tb>	n-n	141,2	952	$4,61\cdot10^{13}$
2.	p-Si<Tb>	p→n	14,9	1042	$4,05\cdot10^{14}$

As can be seen in Table 1, the resistivity of the control samples decreased during prolonged heat treatment. Similarly, the resistivity in the n-Si Tb samples increased after doping with terbium. In contrast, the p-type Si Tb samples showed a decrease in resistivity. However, the mobility of charge carriers also increased.

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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