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PROPERTIES OF SINGLE CRYSTAL SILICON DOPED WITH VANADIUM

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The paper reports the sharp increase in resistivity and the conductivity change (type) in the single-crystal silicon sample doped with vanadium. The electrical and optical properties of single-crystalline silicon were determined Hall- and four-probe measurements and infrared (IR-) spectroscopy. Relative resistance, charge carrier concentration, mobility, and concentration of optically active oxygen and carbon in the samples were determined layer-by-layer. It is shown that in silicon samples doped with vanadium the concentration of optically active oxygen atoms tends to reduce.
Keywords: *Silicon; Vanadium; Diffusion; Resistivity; Optically active; Oxygen; Carbon*
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INTRODUCTION

The proposed technique of doping silicon with vanadium could possibly be used for the production of microcircuits, thus improving the physical parameters of the processed samples and ensuring production of sensitive diodes.

As is known, doping of silicon with impurity atoms that create deep levels leads to the formation of a defect structures in the silicon crystal lattice, and integrated circuits based on silicon doped with transition elements are traditionally characterized by robust long-term performance characteristics [1-2]. Transition elements embedded in silicon play a significant role by gettering the outer electronic shells of impurity atoms and intrinsic atoms, and have high chemical activity. However, it was earlier mentioned that in silicon they are mostly in electrically inactive states [3-4]. However, the mechanisms of these physical phenomena, depending on the type of impurity atoms, environment, chemical composition and structure of these microformations, still remain unclear.

EXPERIMENTAL AND RESEARCH METHODS

The study shows that in the original single-crystalline silicon grown by the CZ- technique, the concentration of oxygen atoms was about ~10^{18} cm^{-3}, while the concentration of carbon atoms approximately 10^{17} cm^{-3}, which were also in electrically inactive state. A series of analysis and studies of manufactured samples is shown in [4-5]. The authors compare various long-term scientific results, the molecular state of vanadium atoms in silicon and their interaction with growing layers.

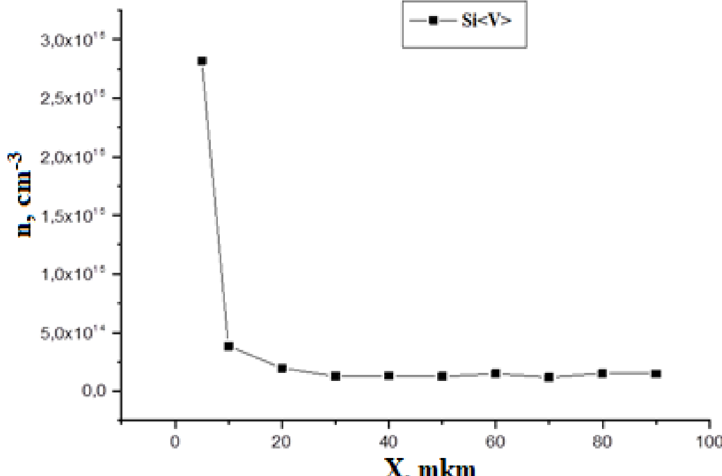

Figure 1. Dependence of charge carrier concentration layer-by-layer

Doping of silicon with vanadium impurity atoms was carried out by implementing the diffusion technique in unvacuumed ampoules at T = 1200^0 C for t = 10 hours and the deposition was induced from a layer of vanadium chloride

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deposited on the surface of single-crystalline silicon. The maximum cooling rate of silicon samples after the diffusion of vanadium atoms was ensured by throwing quartz ampoules into coolant oil, the cooling rate of which $\upsilon_0 \approx 300$ K/s. Minimum cooling rate was $\upsilon_0 \approx 25$ K/s and was ensured after the electric furnace KSL-1075-1 has been turned off. As can be seen from Fig. 1, the charge carrier concentration (n) decreases depending on the penetration depth (x). The charge carrier concentration decreases across the depth of 20 µm from the sample surface, and then a stabilization of the charge carrier concentration is observed.

It was found that the doping Si with V at a diffusion temperature of T_d=900-1000 ^{0}C practically does not change the concentration of n-Si charge carriers.

Table 1. Reference Si sample

Si	Charge carrier concentration, n (cm^{-3})	Carriers mobility, µ (cm^2/Vs)	Specific resistance of samples, ρ (Om·cm)	Conductivity type (type)
	$1.402\cdot10^{14}$	$9.855\cdot10^2$	$5.016E\cdot10^1$	n

It is known that various high-temperature heat treatments (HHT) lead to changes in the defects structure of single-crystalline silicon. In this case, one can witness the process of assembly of various associated states of technological impurities (for example, oxygen atoms in silicon). Depending on the processing temperature, compounds of the SiO_x type are also formed on the silicon surface [5-6].

During the study, the results of the electrophysical parameters of doped silicon samples diffused for 10 hours at a constant temperature T=1200°C are presented in Table 2.

Table 2. Electrophysical parameters of Si<V> diffusion samples

№	Thickness of the removed layer, X (mk)	Carrier mobility, µ (cm^2/Vs)	Specific resistance of samples, ρ (Om·cm)	Conductivity type (type)
1	5	$3.852\cdot10^1$	$5.748\cdot10^1$	p
2	10	$3.869\cdot10^2$	$4.171\cdot10^1$	p
3	20	$7.881\cdot10^2$	$4.023\cdot10^1$	p
4	30	$8.839\cdot10^2$	$5.484\cdot10^1$	n
5	40	$8.798\cdot10^2$	$5.376\cdot10^1$	n
6	50	$8.597\cdot10^2$	$5.839\cdot10^1$	n
7	60	$8.311\cdot10^2$	$5.019\cdot10^1$	n
8	70	$9.676\cdot10^2$	$5.422\cdot10^1$	n
9	80	$8.921\cdot10^2$	$4.594\cdot10^1$	n
10	90	$8.707\cdot10^2$	$4.837\cdot10^1$	n

RESULTS AND DISCUSSION

The authors assume that the resistivity ρ of deep layers of the surface area of the resulting structure does not change sharply, and secondly, it is characterized by an almost flat distribution of resistivity ρ across the bulk of the silicon sample [7-8].

During the study, the resistivity of the starting samples was up to 50 Ohm·cm, and the thickness of the mechanically polished samples was 1.5 mm. The concentration of the optically active oxygen atom is $N_o^{opt}\approx9\cdot10^{17}$ cm^{-3} and the carbon concentration $N_c^{opt}\approx7.3\cdot10^{17}$ cm^{-3}, according to IR-absorption spectra at 1100 cm^{-1} (oxygen band area) and 610 cm^{-1} (carbon band area). Infrared absorption spectrum at 300 K according to a two-beam scheme, infrared spectra FSM-2201 operating in the range 370÷7800 cm^{-1} a spectrometer was used to determine the optically active oxygen (N_0^{opt}) carbon (N_c^{opt}) at room temperature [7-11]. IR-absorption spectra were measured for oxygen at 1106 cm^{-1} (9.1 µm) (Fig. 2b). For carbon, IR-absorption spectra were measured in the range 607 - 620 cm^{-1} (Fig. 2a).

The concentration of optically active oxygen atoms and the concentration of optically active carbon atoms were analyzed using the following equations:

$$N_{\text{o}}^{opt} = 3.3\cdot10^{17}\cdot\frac{1}{d}\cdot ln\frac{I}{I_0} \quad (1)$$

$$N_{\text{c}}^{\text{опт}} = 1.1\cdot10^{17}\cdot\frac{1}{d}\cdot ln\frac{I}{I_0} \quad (2)$$

I and I_0 are intensities of incident and transmitted light, *d* is the thickness of the sample. 1- concentration of optically active oxygen was determined by the following equation:

1. *n-Si (control sample),* $N_{\text{o}}^{opt} = 3.3\cdot10^{17}\cdot\frac{1}{d}\cdot ln\frac{I}{I_0} = 9\cdot10^{17}$ *cm^{-3}*
2. *n-Si<V>,* $N_0^{opt} = 3.3\cdot10^{17}\cdot\frac{1}{d}\cdot ln\frac{I}{I_0} = 8.3\cdot10^{17}$ *cm^{-3}*
3. $\Delta N_{\text{o}}^{opt} = N_{\text{o}}^{opt\,(control)} - N_{\text{o}}^{opt\,(V)} = 9\cdot10^{17} - 8.3\cdot10^{17} = 0.7\cdot10^{17}$ *cm^{-3}.*
4. $k = \frac{\Delta N_{\text{o}}^{opt}}{N_{\text{o}}^{opt\,(control)}}\cdot 100\ \%$

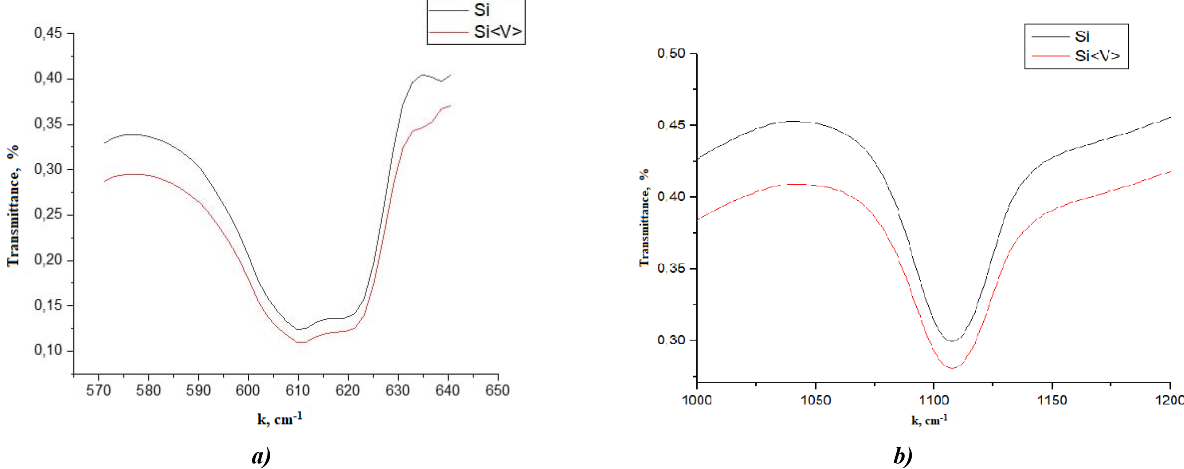

Figure 2. IR-absorption spectrum. a) N_c^{opt}, b) N_O^{opt}, 1 – high spectrum (n-Si) for the reference sample. 2 – for the lower spectrum (n-Si<V>)

Analysis of these results shows that in Si with *n*- and *p*-type vanadium, a decrease in the concentration of optically active oxygen by 8-10% was observed compared to reference samples that had undergone heat treatment under similar conditions. The IR-absorption spectra of optically active carbon at a wavelength of λ=16.4 µm were also studied.

1. *n-Si (control sample),* $N_c^{opt} = 1.1 \cdot 10^{17} \cdot \frac{1}{d} \cdot ln\frac{I}{I_0} = 7.3 \cdot 10^{17}$ *cm*$^{-3}$
2. *n-Si<V>,* $N_c^{opt} = 1.1 \cdot 10^{17} \cdot \frac{1}{d} \cdot ln\frac{I}{I_0} = 7.1 \cdot 10^{17}$ *cm*$^{-3}$
3. $\Delta N_c^{opt} = N_c^{opt\,(control)} - N_c^{opt\,(V)} = 7.3 \cdot 10^{17} - 7.1 \cdot 10^{17} = 0.2 \cdot 10^{17}$ *cm*$^{-3}$.
4. $k = \frac{\Delta N_c^{opt}}{N_c^{opt\,(control)}} \cdot 100\ \%$

In reference samples and doped samples, a decrease in the concentration of optically active carbon by 2-3% was observed [12-16]. In particular, the results of measurements of IR-absorption spectra of starting silicon samples, of the doped silicon in the course of growth from solution and after various heat treatments show that the concentration of optically active oxygen in Si<V> and vanadium increase as a result high-temperature heat treatment of the sample.

CONCLUSIONS

Thus, it has been shown that doping Si with vanadium atoms leads to a decrease in the concentration of optically active oxygen N_O^{opt} by 8÷10 % depending on the concentration of introduced vanadium impurity atoms. The above proves that we are possibly seeing the interaction of vanadium atoms with oxygen atoms in the bulk of silicon. It has been established that preliminary heat treatments of starting silicon samples at T = 1200°C for t = 12 hours leads to the deposition of oxygen in parallel by forming SiO_2 molecules. In this case, the concentration of optically active carbon N_c^{opt} decreases by 2÷3 %. Additional V atoms in pre-heat-treated silicon led to a decrease in N_O^{opt} by 10÷15 %. This is due to the peculiarities of the interaction of V atoms with SiO_2 molecules. It is shown that *p-Si <HT+V>* samples also exhibit an increase in ρ after doping with vanadium atoms, but it is several times smaller compared to *p-Si<V>* samples.

It's worth mentioning that when exposed to IR-radiation (wavelength of λ=16.4 microns when silicon single crystals are transparent), absorption depends only on chemical composition, structure and oxygen concentration. In order to find out the clear mechanism of how vanadium atoms do influence the concentration and size of electroactive centers in silicon, as well as establishing the influence of boundary and surface states on the observed phenomena might require additional research into the subject.

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ВЛАСТИВОСТІ МОНОКРИСТАЛІЧНОГО КРЕМНІЮ, ЛЕГОВАНОГО ВАНАДІЄМ

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У статті повідомляється про різке збільшення питомого опору та зміни (типу) провідності в зразку монокристалічного кремнію, легованого ванадієм. Електричні та оптичні властивості монокристалічного кремнію були визначені вимірюваннями Холла та чотирьох зондів та інфрачервоною (ІЧ) спектроскопією. Відносний опір, концентрацію носіїв заряду, рухливість та концентрацію оптично активного кисню та вуглецю в зразках визначали пошарово. Показано, що в легованих ванадієм зразках кремнію концентрація оптично активних атомів кисню має тенденцію до зменшення.

Ключові слова: *кремній; ванадій; дифузія; питомий опір; оптично активний; кисень; карбон*