

## STUDY OF THE INTERACTION OF EUROPIUM WITH OXYGEN IN SILICON

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### ABSTRACT

The interaction of europium atoms with technological impurities (oxygen and carbon) in silicon was studied by infrared spectroscopy. It is established that the diffusion of europium in Si leads to a decrease in the concentration of optically active oxygen  $N_{O}^{opt}$  for 20 ÷ 30 %. A partial recovery of  $N_{O}^{opt}$  at the subsequent high-temperature treatment was found, which is associated with the decay of the supposed

complexes of europium atoms with technological impurities and activation of europium atoms.

**KEYWORDS:** Silicon, europium, technological impurities, oxygen, carbon, diffusion, doping.

### INTRODUCTION

It is known that the impurities of rare earth elements, chemically active and prone to complexation, even at low concentrations, introduced in silicon during growth are in its lattice in electrically neutral states. In addition, impurities of rare earth elements, without showing electrical activity, interact with various uncontrolled impurities in silicon.<sup>[1-2]</sup> It was found the interaction of atoms Ho, Sm, Gd with carbon in silicon. It is shown that the interaction of rare-earth elements impurities with oxygen occurs in the process of growing from the melt, while the concentration of oxygen in the samples is reduced by adding rare-earth elements to the silicon melt.<sup>[3-4]</sup> From the results of numerous studies it is known that

the doping of silicon rare earth elements significantly changes its properties. In work<sup>[5]</sup> it was found that the doping of silicon Ho, Yb and Er increases stability of its basic electrophysical parameters to influence of ionizing radiation that is connected with presence of metal inclusions of rare earth elements which are effective drains for vacancies. It was also found that rare earth elements also influence the thermal stability of silicon.<sup>[6]</sup>

## MATERIALS AND METHODS

The aim of this work was to study the interaction of europium atoms with technological impurities - oxygen and carbon in silicon, which are always present in the crystal lattice at high concentrations up to  $10^{17} \div 10^{18} \text{ cm}^{-3}$  using infrared spectroscopy.

As the source of samples used were n-Si and p-Si grown by the Czochralski method with concentrations of optical active oxygen atoms  $N_{\text{O}}^{\text{opt}} = 4.3 \cdot 10^{17} \div 1.4 \cdot 10^{18} \text{ cm}^{-3}$  and optical active carbon atoms  $N_{\text{C}}^{\text{opt}} = 2.2 \cdot 10^{16} \text{ cm}^{-3}$ . The resistivity of the initial samples was  $1 \div 60 \text{ Ohms} \cdot \text{cm}$ , the thickness of the polished samples, depending on the task, was  $1 \div 1.5 \text{ mm}$ . The evaluation of the content of oxygen  $N_{\text{O}}^{\text{opt}}$  and carbon  $N_{\text{C}}^{\text{opt}}$  was carried out on the spectra of infrared absorption in the area of  $1100 \text{ cm}^{-1}$  (oxygen band at  $9.1 \text{ }\mu\text{m}$ ) and  $610 \text{ cm}^{-1}$  (carbon band at  $16.4 \text{ }\mu\text{m}$ ), measured on the infrared spectrophotometer Specord - IR-75 in the two-beam scheme at 300 K by formulas:

$$N_{\text{O}}^{\text{opt}} = 3.3 \cdot 10^{17} \cdot 1/d \cdot \ln I / I_0$$

$$N_{\text{C}}^{\text{opt}} = 1.1 \cdot 10^{17} \cdot 1/d \cdot \ln I / I_0$$

Where  $I$  and  $I_0$  are the incident and transmitted light intensities,  $d$  is the thickness of the samples studied. The polished oxygen-free silicon of the same thickness as the test sample with  $N_{\text{O}}^{\text{opt}} \leq 10^{16} \text{ cm}^{-3}$ ,  $N_{\text{C}}^{\text{opt}} = 5 \cdot 10^{15} \text{ cm}^{-3}$  was used as a reference sample.

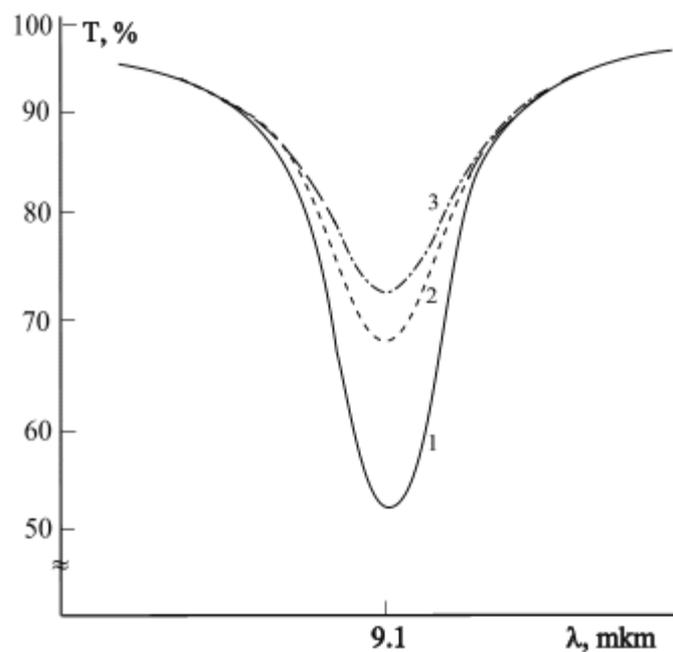
After measuring  $N_{\text{O}}^{\text{opt}}$  and the  $N_{\text{C}}^{\text{opt}}$  in the original samples Si they introduced impurity Eu by diffusion method of vacuum deposited layer of metal europium high purity in the temperature range of  $900 \div 1200^\circ\text{C}$ . After the diffusion of europium in these samples was measured again  $N_{\text{O}}^{\text{opt}}$  and the  $N_{\text{C}}^{\text{opt}}$  by the method of infrared absorption.

## RESULTS AND DISCUSSION

The results of infrared absorption spectra measurements at wavelength  $\lambda = 9.1 \text{ }\mu\text{m}$  corresponding to the absorption of optically active oxygen are shown in Fig. 1 (curves 2 and 3), the analysis of which shows that after the introduction of the atoms of europium in Si

there was a decrease in the concentration of optically active oxygen by 20 ÷ 30 % compared with the control samples, heat-treated under the same conditions as the europium diffusion (Fig.1, curve 1). The analysis of these dependencies shows that the effect of reducing the concentration of optically active oxygen  $N_{O}^{opt}$  depends on temperature diffusion, that is concentration of atoms introduced europium  $N_{Eu}$ : the more  $N_{Eu}$ , the more the reduction in  $N_{O}^{opt}$ .

Measurements of the infrared absorption spectra at the wavelength of  $\lambda = 16,4 \mu\text{m}$  corresponding to the absorption of the optically active carbon in the Si showed that in the control and diffusion-doped with europium samples effect of reducing the concentration of optically active carbon  $N_C^{opt}$  was not observed.



**Fig. 1: The spectra of infrared absorption in the test samples of n-Si and doped samples n-Si<Eu>:**

**1 - the test samples**

**2 -  $T_{diffusion} = 1000^{\circ}\text{C}$**

**3 -  $T_{diffusion} = 1200^{\circ}\text{C}$**

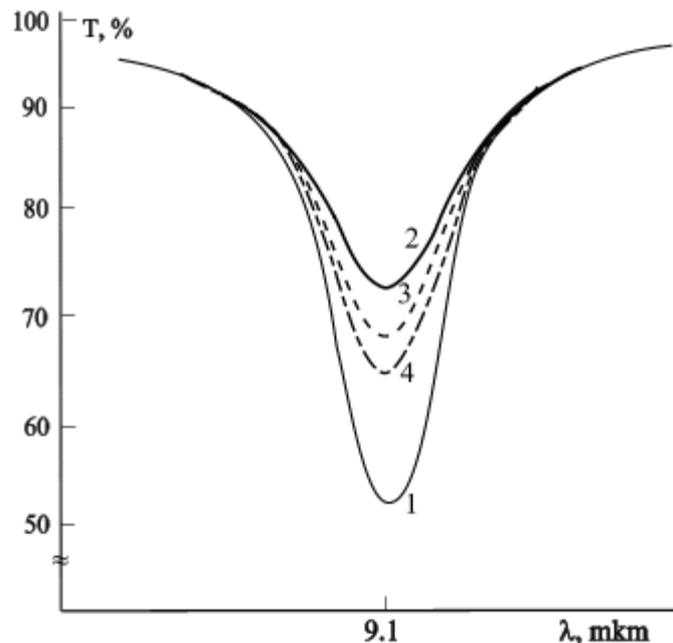
We have also investigated the spectra of infrared absorption in silicon samples doped by europium in the process of growing from a melt (Fig.2, curve 2) and control samples of silicon (Fig.2, curve 1). The analysis of these dependences shows that the doping of silicon with impurity of europium during melt growth, as well as diffusion doping, leads to a significant decrease in the concentration of optically active oxygen  $N_{O}^{opt}$ .

The influence of different cycles of high-temperature treatments on the properties of n-Si doped with europium (n-Si<Eu><sub>grown</sub>) was also studied.

Subsequent high-temperature processing of the samples n-Si<Eu><sub>grown</sub> in the temperature range of 900÷1200°C leads to an increase in the concentration of optically active oxygen  $N_{O}^{opt}$  to 10-15%, that is, there is a partial recovery of  $N_{O}^{opt}$ .

The results of the measurements of the of infrared absorption spectra before and after heat treatment at temperatures of 900÷1200°C indicate an increase in the concentration of optically active oxygen in the samples n-Si<Eu><sub>grown</sub> as a result of high temperature treatments. Typical spectra of infra-red absorption of samples before and after heat treatment at 1000°C are shown in figure 2 (curves 1 and 2), from which it can be seen that heat treatment of n-Si<Eu><sub>grown</sub> samples at 1000°C followed by rapid cooling leads to an increase in the concentration of optically active oxygen by 8 ÷10%.

With increasing treatment temperature, the effect of increasing  $N_{O}^{opt}$  more and after heat treatment at  $T=1200^{\circ}C$  followed by rapid cooling (quenching)  $N_{O}^{opt}$  reaches 15÷20%.



**Fig. 2:** Spectra of infrared absorption in the control samples n-Si (1), samples of n-Si<Eu> doped at growing (2) and subjected to heat treatment (3, 4),  $T_{\text{heat treatment}}$ : 3 - 1000°C, 4 - 1200°C.

Preliminary experiments carried out by us with the help of metallographic microscope and local X-ray microanalyzer showed that the studied samples of silicon doped by europium atoms at growth observed large precipitates, whose dimensions ranged from 30 microns to 300 microns in samples.

It can be assumed that the detected precipitates contain europium atoms and technological impurities, i.e. oxygen and carbon atoms, which are always present in the silicon melt. Apparently, the heat treatment of silicon samples with europium in the temperature range 900÷1200°C leads to the disintegration of these precipitates, as a result of which the concentration of optically active oxygen increases and several deep levels are formed due to the activation of europium atoms. It should be noted that no changes were detected in the absorption band of optically active carbon at 16.5 μm.

## CONCLUSIONS

Thus, it was found that the doping of silicon with rare earth impurity by europium (regardless of the method of doping) leads to a decrease in the concentration of optically active oxygen. A partial recovery of  $N_{O}^{opt}$  was found, followed by the fact that it is associated with the decay of the proposed complexes of Eu atoms and technological impurities and the activation of europium atoms. It is shown that the effect of reducing the concentration of optically active oxygen  $N_{O}^{opt}$  depends on the concentration of atoms introduced by europium: the more  $N_{Eu}$ , the greater the reduction in the value of  $N_{O}^{opt}$ . The effect of reducing the concentration of optically active carbon  $N_{C}^{opt}$  was not observed. Discovered that various high-temperature treatment at 900÷1200°C of n-Si, doped with europium at growth lead to a partial recovery of the concentration of optically active oxygen -  $N_{O}^{opt}$  increase by 10-15%.

Large precipitates of europium atoms with sizes ranging from 30 μm to 300 μm in samples of n-Si<Eu> were found.

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