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# Deep Level Transient Spectroscopy of Silicon, Doped by Zirconium

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Abstract: By means of methods transient capacitance spectroscopy of deep levels and photo-capacitance studied the formation of defects in silicon, doped Zirconium. Discovered that diffusive introduction of zirconium into the silicon leads to the formation of three deep levels with fixed ionization energies of Ec-0.22 eV, Ec-0.42 eV and Ev+0.30 eV, and dominate the last two levels. It is established that the efficiency of the formation of deep centers associated with the atoms of zirconium increases with temperature diffusion and the cooling rate after diffusion. Keywords: spectroscopy, silicon, defect, doping of the impurity, Zirconium.

### I. INTRODUCTION

It is known that the formation of the defect structure of silicon is determined by the presence of specially introduced impurities, creating in the forbidden zone of silicon, a number of deep levels (DL) and has a significant influence on the electrophysical parameters of Si. To control parameters of silicon in recent years have increasingly used nontraditional doping impurities [1-4], examples of such impurities are refractory elements - atoms of hafnium, tungsten, zirconium, tantalum, etc. The purpose of this work was to study the energy spectrum of defects in silicon, doped with one of these elements, zirconium introduced in the Si diffusion method. The studies were conducted using nonstationary capacitance spectroscopy of deep levels DLTS and photo-capacitance .

### II. EXPERIMENTAL SETUP

Doping of silicon by impurity of zirconium was carried out by diffusion method in a vacuum evaporated layer of metal Zr of high purity in the temperature range of  $1000 \div 1250^{\circ}$ C for  $1 \div 50$  hours. As control was used the samples of n - Si and p-Si heat-treated at the same temperature and time as the introduction of zirconium into the silicon.

For the doping used were n-Si with initial resistivity of 1 to 300  $\Omega$ ·cm p-Si from 1 to 300  $\Omega$ ·cm, the cooling rate of the samples after the diffusion of zirconium was varied from 0.1° C/s to 40-70°C/s.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

The measurement results showed that in all samples n-Si after doping with zirconium to an increase in magnitude of the resistivity. In the samples p-Si of resistivity remains almost unchanged. For the samples Si, diffusion-doped with Zirconium, as well as subjected to control heat treatment were measured DLTS spectra and photo-capacitance. For carrying out capacitive measurements from the uncompensated crystals produced Schottky barriers by evaporation in a vacuum of gold on n-Si and antimony – on p-Si according to the technology described in [5]. As the ohmic contact is a chemically deposited Nickel or antimony evaporation.

DLTS spectra were measured in the regimes of constant capacitance and constant voltage [6, 7], and measurements of the spectra of photo-capacitance was carried out according to conventional techniques described in [7].

The dependence  $1/C^2 = f(V_{reverse})$  determined from capacitance-voltage characteristics of all investigated diodes was linear. The concentration of ionized centers in the space charge layer in the diodes of the n-Si<Zr>, and also in p-Si<Zr>, determined on dependence  $1/C^2 = f(V_{obp})$  at 300K, in good agreement with the concentration of acceptors in the initial silicon.

From measurements of the DLTS spectra of samples Si, diffusion-doped with Zirconium, as well as control samples, subjected to heat treatment (without any impurity of Zr) was determined the energy spectrum of deep levels. In Fig.1 shows the DLTS spectra of the samples n-Si and p-Si doped with zirconium at 1000°C and 1250°C followed by rapid cooling.



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Fig.1.DLTS spectra of the samples n-Si and p-Si doped with Zr at 1000°C C and 1250°C (curve 1a, 2a), control samples (curve 3).

Processing of these spectra and the calculations show that the diffusion introduction of atoms of zirconium in n-Si and p-Si leads to the formation of several deep levels with fixed energy of ionization. In samples n-Si< Zr> was observed deep levels with parameters  $E_c - 0.22 \text{ eV}$ ,  $\sigma_n = 2 \cdot 10^{-15} \text{ cm}^2$  and  $E_c - 0.42 \text{ eV}$ ,  $\sigma_n = 7 \cdot 10^{-16} \text{ cm}^2$  (Fig.1, curve 1 and 1a) and the samples p-Si<Zr> are observed deep levels  $E_v + 0.30 \text{ eV}$ ,  $\sigma_p = 5 \cdot 10^{-15} \text{ cm}^2$  (Fig.1, curve 2 and 2a).

Analysis of measured DLTS spectra of the samples n-Si<Zr> and p-Si<Zr> shows that the presence of Zr in Si leads to the formation of deep levels with fixed energy of ionization, the dominant ones are the last two levels. It is established that the efficiency of the formation of deep centers associated with the atoms of zirconium increases with temperature diffusion  $T_{diff}$  and the cooling rate after diffusion  $v_{cool}$ : the more  $T_{diff}$  and  $v_{cool}$ , the greater the concentration of deep levels of zirconium.

Simultaneous measurements of the spectra of photo-capacitance showed (Fig. 2) that in the doped samples, observed relaxation capacity in the energy region  $h\nu \sim 0.22$ , 0.42 and 0.30 eV. This energy range coincides with the measurements of the DLTS spectra, which suggests that the thermal and optical ionization energy of the detected levels do not differ.



Fig.2. Typical spectra of the photo-capacitance (1) and photo-induced capacitance (2) samples of n-Si doped with Zr .

To determine the deep levels located in the lower half of the forbidden zone in the n-Si $\langle Zr \rangle$ , has been measured photo-induced capacitance. For this diode from the base was illuminated by a long time light with  $h\nu \ge 1.4$  eV. Measurement induced photo capacity showed that in the lower half of forbidden zone was discovered the only level



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with ionization energy  $E_v+0.30$  eV (Fig.3, curve 2). On the kinetics of filling levels by flow of minority carriers was measured the capture cross section of holes at the levels  $E_v+0.30$  eV, which are associated with zirconium in silicon. The capture cross section of Zr at these levels were determined based on lgN=f(t), it was  $4.10^{-17}$  cm<sup>2</sup>.

Parallel measurements of the spectra of DLTS and of photo-capacitance of the control heat treated samples of n-Si have shown that they have only a level with an ionization energy of  $E_c$ -0.22 eV, its concentration was of the order of  $N_{DL} = 10^{14}$  cm<sup>3</sup>, which is much higher than in the samples doped with zirconium. Hence, we can conclude that the atoms of zirconium in silicon are only the last two levels, namely the levels with the ionization energy  $E_c$ -0.42 eV and  $E_v$ +0.30 eV, and an  $E_c$ -0.22 eV is a defect in the heat treatment

#### IV. CONCLUSIONS

Thus, we can conclude that diffusive introduction of zirconium into the silicon leads to the formation of three deep levels with parameters  $E_c - 0.22 \text{ eV}$ ,  $\sigma_n = 2 \cdot 10^{-15} \text{ cm}^2$  and  $E_c - 0.42 \text{ eV}$ ,  $\sigma_n = 7 \cdot 10^{-16} \text{ cm}^2$  in n-Si< Zr>, the level  $E_v + 0.30 \text{ eV}$ ,  $\sigma_p = 5 \cdot 10^{-15} \text{ cm}^2$  in p - Si< Zr>. It is established that only the last two levels, namely the levels with the ionization energy  $E_c$ -0.42 eV and  $E_v$ +0.30 eV, associated with the atoms of zirconium and silicon, and an  $E_c$ -0.22 eV is a defect of the heat treatment.

The efficiency of the formation of deep centers associated with the Zr atoms increases with increasing temperature diffusion  $T_{diff}$  and the cooling rate after diffusion  $v_{cool}$ : the more  $T_{diff}$  and  $v_{cool}$ , the greater the concentration of deep levels relating with Zr.

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