



## DEEP LEVELS OF ZIRCONIUM IN SILICON AND SILICON STRUCTURES

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### ABSTRACT

By means of methods transient capacitance spectroscopy of deep levels studied the formation of defects in silicon and silicon structures, doped Zirconium. Discovered that diffusive introduction of zirconium into the silicon leads to the formation of three deep levels with fixed ionization energies of  $E_c-0.22$  eV,  $E_c-0.42$  eV and  $E_v+0.30$  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.

### INTRODUCTION

In recent years, in the manufacture of many semiconductor devices to reduce the lifetime of minority carriers to increase the performance of devices used impurity tight-fusible elements to reduce the lifetime of minority carriers to increase quick-action devices,<sup>[1-2]</sup> the wide use of metal silicides in modern technologies again evoked the interest in refractory alloys (titanium, zirconium, hafnium and others). It is known that for the monitored control parameters of the silicon are increasingly being used in unconventional doping impurities,<sup>[3-4]</sup> examples of such impurities are refractory elements – atoms of hafnium, tungsten, zirconium, tantalum and others. Along with this data on the behavior of impurities of refractory elements

in silicon, energy levels, formed by these impurities in the forbidden gap of silicon do not exist.

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 deep levels transient spectroscopy (DLTS).

## MATERIALS AND METHODS

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÷1250°C for 1÷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 Ω·cm p-Si from 1 to 300 Ω·cm, the cooling rate of the samples after the diffusion of zirconium was varied from 0.1° C/s to 40-70°C/s.

## RESULTS AND DISCUSSION

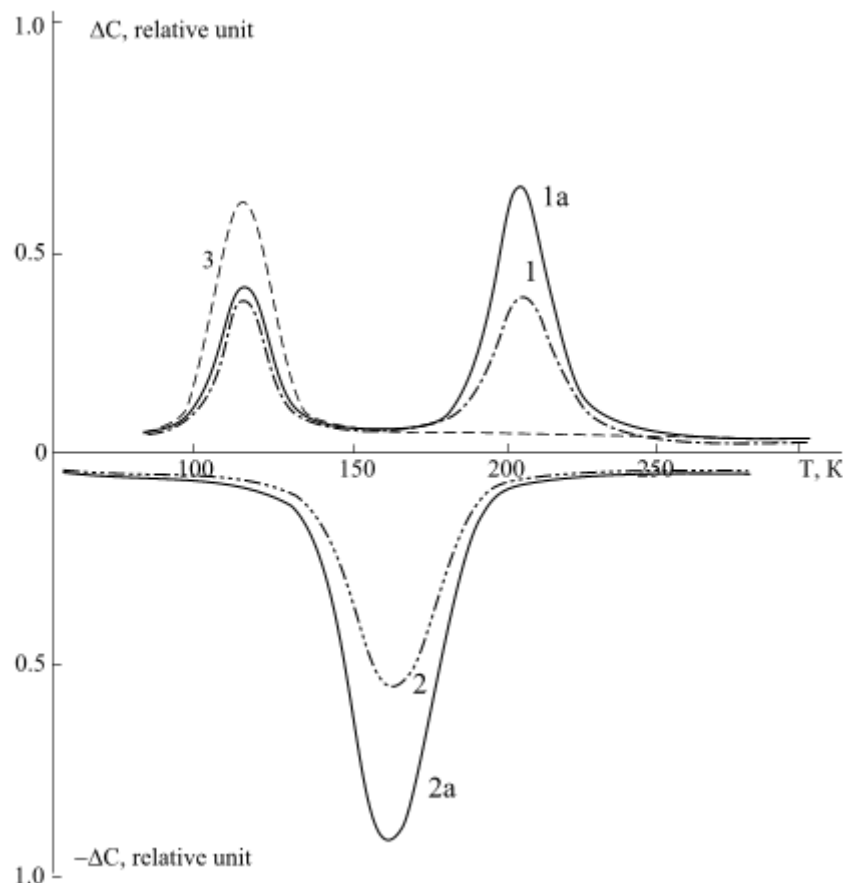
The studies were conducted using deep levels transient spectroscopy (DLTS). For carrying out capacitive measurements from the uncompensated crystals produced Schottky barriers by evaporation in a vacuum of gold on n-Si and antimony on p-Si according to the technology described in.<sup>[5]</sup> As the ohmic contact is a chemically deposited Nickel or antimony evaporation.

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. DLTS spectra were measured in the regimes of constant capacitance and constant voltage.<sup>[6,7]</sup>

The dependence  $1/C^2 = f(V_{\text{reverse}})$  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  $1/C^2 = f(V_{\text{reverse}})$  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. Processing of these spectra and 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 energy of ionization  $E_c-0.22$  eV and the capture cross section of charge carriers  $\sigma_n = 2 \cdot 10^{-15}$  cm<sup>2</sup> and  $E_c-0.42$  eV,  $\sigma_n = 7 \cdot 10^{-16}$  cm<sup>2</sup> (Fig.1, curve 1 and 1a) and the samples p-Si<Zr> are observed deep levels  $E_v+0.30$  eV,  $\sigma_p = 5 \cdot 10^{-15}$  cm<sup>2</sup> (Fig.1, curve 2 and 2a).



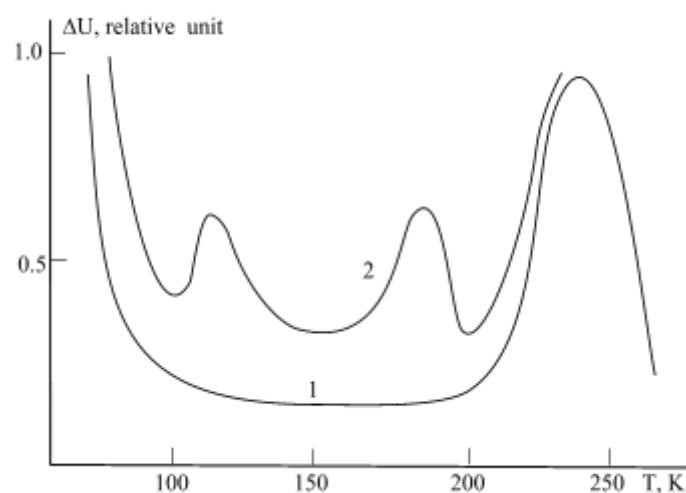
**Fig.1: DLTS spectra of the samples n-Si and p-Si doped with Zr at 1000°C and 1250°C (curve 1a, 2a), control samples (curve 3).**

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.

Measurements of the spectra of DLTS 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  $N_{DL} = 10^{14} \text{ cm}^{-3}$ , 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. Was studied also the influence of atoms of zirconium on the properties of silicon structures, such as metal-insulator semiconductor (MIS).

Measurements of the spectra of DLTS in MIS structures based on silicon doped Zirconium (Fig.2, curve 2) and control structures (Fig.2, curve 1) showed that the spectra of doped samples are observed 2 peaks with maxima at temperatures of  $T_{max} = 110$  K and  $T_{max} = 180$  K, while in the control samples, these peaks are not detected. Numerical calculations of the parameters of the defects based on these peaks showed that the peak with a maximum at  $T = 110$  K corresponds to a level with an ionization energy of  $E_c-0.23$  eV, and the peak at  $T = 180$  K - level with an ionization energy  $E_c-0.42$  eV.



**Fig. 2: Spectra of CC-DLTS in MIS-structures based on silicon doped Zirconium (curve 2) and test MIS-structures (curve 1).**

To identify the nature of these defects with certain impurities in the investigated MIS-structures was removed the oxide layer and they produced Schottky barriers. As a Schottky

barrier on a substrate of n-Si<Zr> evaporation gold, and the ohmic contact were deposited antimony in a high vacuum.

Measurement of DLTS spectra obtained on barriers showed that in all samples there is a recharge two deep levels in the upper half of the forbidden zone of Si with energies of ionization  $E_c-0.23$  eV and  $E_c-0.42$  eV. They coincide with the levels of atoms of zirconium in silicon.

## CONCLUSIONS

Thus, we can conclude that diffusive introduction of zirconium into the silicon leads to the formation of three deep levels with parameters  $E_c-0.22$  eV,  $\sigma_n = 2 \cdot 10^{-15}$  cm<sup>2</sup> and  $E_c-0.42$  eV,  $\sigma_n = 7 \cdot 10^{-16}$  cm<sup>2</sup> in n-Si<Zr>, the level  $E_v+0.30$  eV,  $\sigma_p = 5 \cdot 10^{-15}$  cm<sup>2</sup> 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 in silicon, and an  $E_c-0.22$  eV is a defect of the heat treatment. In Fig.2 shows spectra of CC-DLTS in MIS-structures with silicon substrate doped Zirconium (curve 2) and test MIS-structures (curve 1).

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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