



### EFFECT OF IMPURITIES OF DIFFICULT MELT ELEMENTS ON THE PHOTSENSITIVITY OF DOPED SILICON

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#### ABSTRACT

The influence of impurities of zirconium and hafnium on the properties of silicon and defines their role in enhancing the photosensitivity of doped silicon. It is shown that structures based on silicon doped as zirconium and hafnium, possess photosensitivity in the range of 3-5 microns, with a maximum  $\lambda_{Si<Zr>}$  = 4.1 microns at room temperature.

**KEYWORDS:** Spectroscopy, silicon, defect, difficult melt impurity, doping, photosensitivity, zirconium, hafnium.

#### INTRODUCTION

Currently, the most efficient from the energy point of view, devices for converting solar energy into electricity are semiconductor photovoltaic cells (solar cells).<sup>[1]</sup> Energy conversion in solar cells based on the photovoltaic effect, which occurs in inhomogeneous semiconductor structures when exposed to solar radiation. The heterogeneity of the structure of solar cells can be obtained by doping the same semiconductor with various impurities (to create p - n junctions) or by combining different semiconductors with varying band gap (creation of heterojunctions).

The conversion efficiency depends on the electrical characteristics of inhomogeneous semiconductor structures, and optical properties of solar cells. Monocrystalline silicon is one of the main materials of solar energy, the rapid development of which determines the requirements for semiconductor materials.<sup>[2]</sup>

Qualitative improvement of the efficiency of photo conversion of silicon solar cells requires a significant increase in perfection of crystal structure. This is because a characteristic feature of semiconductor materials is the sharp dependence of their fundamental electrical properties not only from the content of the impurities, but also from the degree of perfection of the crystal structure.

## MATERIALS AND METHODS

The aim of this work is to study the influence of impurities of difficult melt elements (zirconium and hafnium) on the electrophysical properties of silicon and their role in enhancing the photosensitivity of doped silicon. The studies were conducted by methods of deep levels transient spectroscopy (DLTS) and photo capacity (FE). The technology of manufacture of Schottky barriers and ohmic contacts, methods of measurement and processing of the DLTS spectra presented in.<sup>[3]</sup>

Silicon doping impurities of zirconium and hafnium was carried out by diffusion method in a vacuum from evaporated layer of Zr and Hf of high purity in the temperature range of  $1000\div 1200^{\circ}\text{C}$  for  $1\div 50$  hours. Sample cooling after the diffusion of impurities was carried out in various ways. As control was used the samples of n- and p-Si heat-treated at the same temperature and time as the introduction of zirconium and hafnium in Si.

## RESULTS AND DISCUSSION

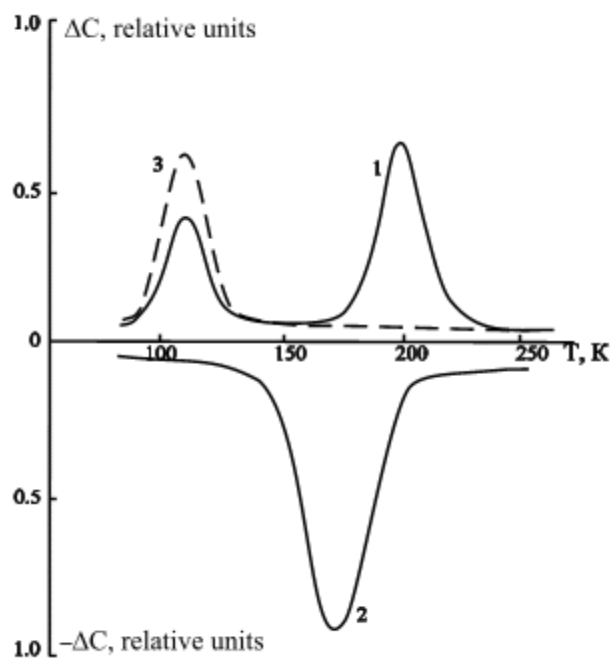
The measurement results showed that in all samples n -Si after doping Zr or Hf, an increase in the magnitude of the resistivity. In the samples p-Si of resistivity remains almost unchanged.

The energy spectrum of deep levels were determined from measurements of the spectra of DLTS and photo-capacitance samples Si, diffusion-doped with zirconium or hafnium, as well as control samples, subjected to heat treatment (without any admixture of Zr or Hf). For measurements of the spectra of photo capacitance and DLTS samples were fabricated diode structures according to the known technique.<sup>[3]</sup> Measurements and processing of spectra are described in details in.<sup>[3,4]</sup>

In Fig.1 shows the DLTS spectra of the samples n -Si<Zr> (curve 1) and p-Si<Zr> (curve 2), diffusion of zirconium was carried out at  $1200^{\circ}\text{C}$  followed by rapid cooling.

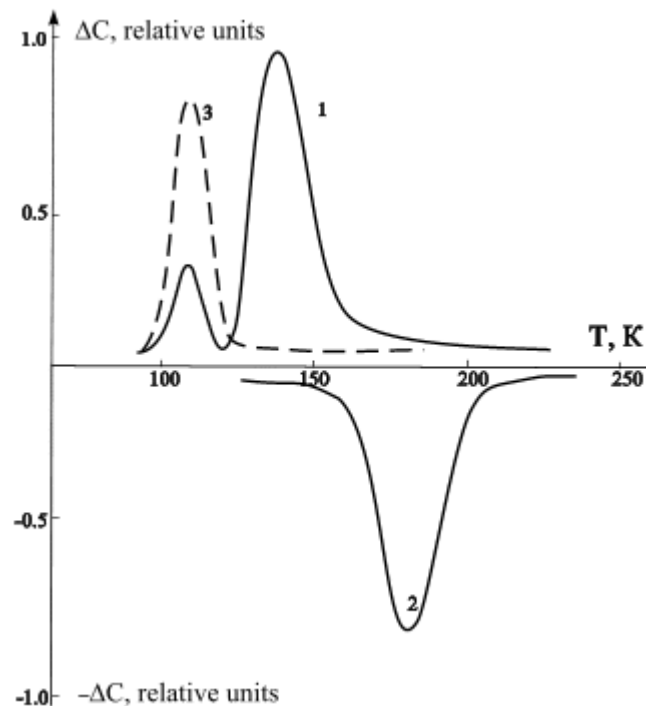
From the analysis of the measured DLTS spectra of the samples n -Si<Zr> and p-Si<Zr>, it follows that the introduction of Zr by diffusion in Si leads to the formation of three deep levels with fixed ionization energies of  $E_c - 0.22$  eV,  $E_c - 0.42$  eV and  $E_v + 0.30$  eV, and dominate the last two levels.

Discovered that the efficiency of the formation of deep centers associated with the atoms of zirconium increases with temperature diffusion  $T_{dif}$  and the cooling rate after diffusion  $v_{cool}$  : the more  $T_{dif}$  and  $v_{cool}$ , the greater the concentration of deep levels Zr.



**Fig. 1: DLTS spectra of the samples n-Si and p-Si doped with Zr 1200°C.**

Measurements of the spectra of CC-DLTS in Schottky diodes based on n-Si<Hf> (Fig.2) showed that in all samples observed recharging two deep levels in the upper half of the forbidden zone of silicon with ionization energies of  $E_c - 0.22$  eV and  $E_c - 0.28$  eV.



**Fig. 2: DLTS spectra of the samples n-Si<Hf> (1), p-Si<Hf> (2) and the control n-Si (3).**

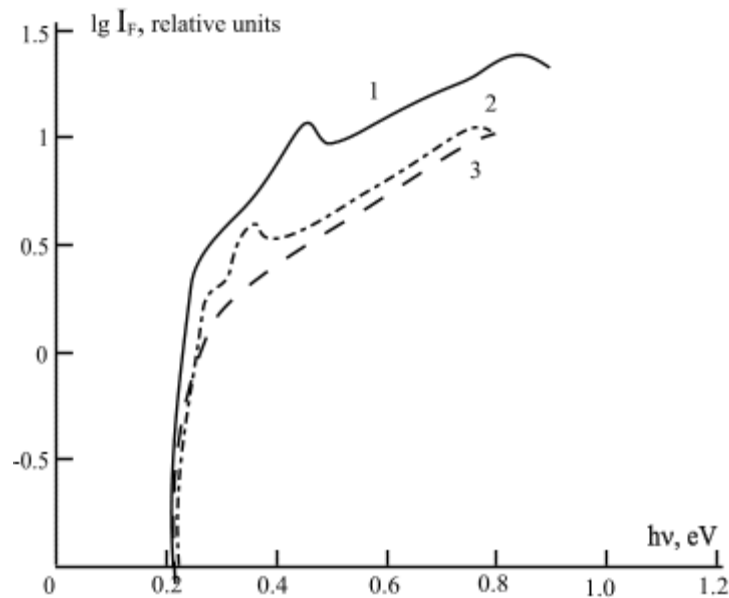
Scanning the entire width of the forbidden zone on these samples by the method of photo capacity found that the spectra induced photo capacity is observed recharge about energy  $h\nu \approx 0.35$  eV. These results were also confirmed using measurements of the spectra of CC-DLTS.

A comparison of the spectra of CC-DLTS and photo-capacitance silicon samples, doped with hafnium control and heat -treated samples showed that the atoms of hafnium diffusion when the introduction of silicon to form two deep-level ionization energies  $E_c - 0.28$  eV and  $E_v + 0.35$  eV.

The analysis of spectra DLTS and photo -capacitance in the control heat treated samples of n-Si (Fig.1 and Fig.2, curve 3) showed that they have only a level with an ionization energy of  $E_c - 0.22$  eV, and its concentration is 1 order of magnitude higher than in samples doped with zirconium or hafnium. A comparison of the data shows that the presence of Zr or Hf atoms in the volume of silicon leads to decreasing concentrations of deep level  $E_c - 0.22$  eV, caused by heat treatment, i.e. leads to a decrease in the efficiency of thermal defect formation in silicon.

The results of the measurements of the spectra of photoconductivity showed that the investigated structures based on silicon doped as zirconium (Fig.3, curve 1), and hafnium

(Fig.3, curve 2) possess photosensitivity in the range of 3-5  $\mu\text{m}$ , with a maximum  $\lambda_{\text{Si}<\text{Zr}>} = 4.1$   $\mu\text{m}$  at room temperature. Based on these structures we created laboratory samples of solar cells with enhanced thermal stability and repeatability of the photo electrical parameters in comparison with similar structures based on Si.



**Fig. 3: Normalized to a constant stream of quanta spectra of photoconductivity in n-Si<Zr> (1), n-Si<Hf> (2) and the control n-Si (3).**

Experiments were conducted to profile the distribution of impurities of zirconium and hafnium in volume of silicon by scanning DLTS spectra on the thickness of the samples and the method of layer -by-layer etching of Si.

As a result of researches it is established that impurities such as Zr and Hf, distributed in volume of silicon uniformly without forming any clusters. Hence it can be concluded that the photovoltaic devices based on Si doped as Zr and Hf, is not observed nonuniform photogeneration, leading to instability of the parameters of silicon solar cells.

## CONCLUSIONS

Thus, analyzing the obtained results we can draw the following conclusions: on the basis of silicon, doped as zirconium and hafnium, it is possible to create solar cells having photosensitivity in the range of 3 -5  $\mu\text{m}$ , with a maximum  $\lambda_{\text{Si}<\text{Zr}>} = 4.1$   $\mu\text{m}$  at room temperature. Note that the resulting structures have high thermal stability, uniform photogeneration and reproducibility of the photovoltaic parameters.

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