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# IMPEDANCE SPECTROSCOPY of p-Si<Pt>, p-Si<Cr> IRRADIATED WITH PROTONS

**Sh.B. Utamuradova[1], D.A. Rakhmanov[1*], A.S. Doroshkevich[2], I.G. Genov[2,3], Z. Slavkova[2,4], M.N. Ilyina[2]**

[1]Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan, Tashkent, Uzbekistan
[2]FLNP, Joint Institute for Nuclear Research, Dubna, Russia
[3]Institute of Electrochemistry and Energy Systems "Acad. Evgeni Budevski"- Bulgarian Academy of Sciences, Sofia, Bulgaria
[4]Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

**Abstract.** In this work, the effect of proton implantation (a dose of $5 \times 10^{14}$ particle/cm$^{-2}$) on the electrical properties of p-type silicon (p-Si) single crystals doped with platinum and chromium was studied using the method of impedance spectroscopy. It has been established that radiation-induced changes in the electrical conductivity of silicon depend significantly on the type of dopant. It is determined that the electrical resistance of silicon as a result of irradiation will increase sharply by several times due to the creation of radiation defects. However, by doping with transition elements (Pt, Cr), its electrical resistance can be reduced. Using an electron microscope, the elemental composition was determined and microphotography were taken on the surface of doped, irradiated silicon samples.

***Keywords:*** *Transition state theory, gas sensor, ethanol detection, density functional theory, silicon, platinum, chromium, doping, diffusion, proton irradiation.*

[*]***Corresponding Author:*** *D.A. Rakhmanov, Institute of Semiconductor Physics and Microelectronics at the National University of Uzbekistan, 20 Yangi Almazar st., Tashkent, 100057, Uzbekistan*
*e-mail: dilmurod-1991@bk.ru*

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## 1. Introduction

Modification of semiconductor materials by beams of light ions, in particular protons, is one of the most promising and actively developing physical and technological methods in recent years. Interest in the implantation of silicon crystals by protons is due to a wide and controllable range of processed depths (from 0.1 μm to 1 mm) and the absence of complex radiation complexes with a high annealing temperature after irradiation. The main three factors affecting the change in the properties of semiconductors after proton irradiation are: a change in the electrical properties of semiconductors, radiation defect formation, and accumulation of hydrogen atoms (Kozlov & Kozlovskiy, 2001; Jafarov *et*

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*al*., 2019).

Modeling, synthesis and research of new functional materials is one of the urgent scientific problems of our time. The microstructure and isovalent impurities determine the functional properties of materials of this class. Therefore, the study of the electrical properties of semiconductors and semiconductor structures, taking into account their real microstructure, is an important and urgent task (Galeeva, 2010; Shehata *et al*., 2023). New materials based on silicon, in particular those containing platinum or chromium (p-Si<Pt>, p-Si<Cr>, respectively) as a dopant (p-type conductivity), have not been sufficiently studied and are of interest for fundamental science and practical applications.

The purpose of this work is to study the effect of proton implantation on the electrical properties of p-Si<Pt>, p-Si<Cr> single crystals using impedance spectroscopy.

The impedancemeter allows to study the electrically conductive properties of materials by recording the spectra of impedance (complex resistance to alternating current) at a constant polarizing voltage. The device can register the active and reactive components of the impedance when an alternating (sinusoidal) voltage with a different fixed signal amplitude is applied to the test sample or system, measure the dielectric characteristics of semiconductor systems, and also has other useful functionalities for researchers (Bhattacharya *et al*., 2021; Pan *et al*., 2020).

Electrochemical impedance spectroscopy (EIS) is one of the most informative methods for the electrochemical study of materials due to its unique ability to separate the kinetics of various stages occurring in electrochemical processes (Stoynov & Vladkova, 2005; Tetelbaum *et al*., 2022). Impedance measurements are performed over a wide frequency range (about nine decades), which makes it possible to observe processes with a large difference in time constants. EIS can be used to isolate and evaluate electronic and ionic conductivities, fast electrochemical kinetics, diffusion and other transport restrictions, as well as the formation and development of new phases.

## 2. Materials and methods

The objects under study were p-type silicon wafers 2×7×14 $mm^3$ in size with a resistivity of 3 Ω cm (KDB-3). The plates were cut from silicon grown by the Czochralski method. Doping of silicon with platinum and chromium was carried out by the diffusion method with deposition of platinum and chromium atoms on the silicon surface in evacuated quartz ampoules at temperatures $T$ = 900-1250 °C for 2-10 hours. Subsequent cooling of the samples occurred using the thermal regimes given in (Utamuradova *et al*., 2019). The concentration of the boron dopant in the initial (before cutting) p-Si single crystals was $2.6\times10^{13}$ - $3.4\times10^{15}$ $cm^{-3}$.

After cleaning, the doped samples were irradiated with 2 MeV protons at a current of 0.5 μA until a dose of $5.1\times10^{14}$ particles/$cm^2$ was obtained using the EG-5 electrostatic accelerator at the Neutron Physics Laboratory of the Joint Institute for Nuclear Research (FLNP JINR).

Studies of the electrical properties of silicon samples were carried out at room temperature (27 °C) on a Sp-200 “BioLogic” impedance meter in a two-electrode cell in the frequency range from 1 Hz to 1 MHz at an excitation signal voltage of 10 mV. Overhead electrodes were made of copper foil, the clamping was carried out using a foam sponge.

Micrographs of the studied samples were obtained using a scanning electron microscope (SEM). To determine the elemental composition of silicon samples, we used the method of X-ray spectral microanalysis using an electron microscope “Tascan Vega3”.

## 3. Results and discussion

On fig. 1 shows the impedance hodographs of an undoped p-Si sample before and after irradiation (hereinafter referred to as “initial”).

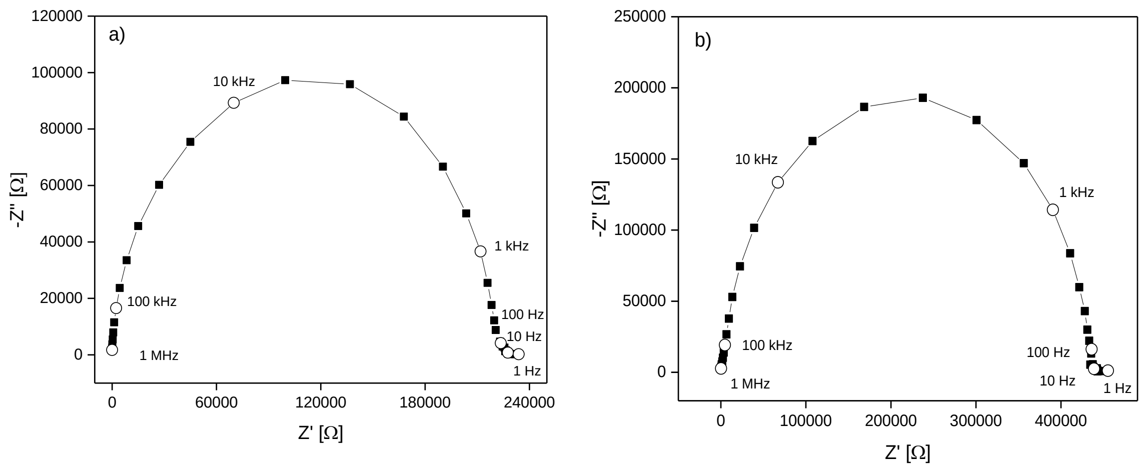


**Fig.1.** Hodographs of the initial p-Si sample. before (*a*) and after (*b*) irradiation

The impedance spectrum (Fig. 1*a*) is in the resistance range 11 Ω - 222 kΩ and has the shape of an arc of a circle, which is typical for the electrode reaction. The section of the diagram in the range from 0 - 11 Ω along the X axis corresponds to the resistance of the electrolyte (Buyanova & Emelyanova, 2008).

The impedance spectrum of the irradiated sample (Fig. 1*b*) has a similar shape and is in the range 206 Ω – 436 kΩ. It can be seen that irradiation in this case led to an increase (by almost a factor of 2) in the resistance of the sample, presumably due to the formation of defects in the crystal lattice (Utamuradova *et al*., 2022a).

On fig. 2 shows the impedance hodographs of p-Si samples doped with Pt before and after irradiation.

A curve in the form of an arc of a circle is observed (Fig. 2*a*) in the range of ohmic resistance values up to 33 kΩ. In the frequency range of about 10 kHz, the shape of the arc is distorted, and in the low-frequency region, the continuity of the curve is lost and a strong scatter of points is observed, which indicates the presence of diffusion limitations associated with the inhomogeneity of the material under study (conduction channels). Irradiation leads to an increase in the ohmic resistance by at least a factor of 3 (up to 98 kΩ, Fig. 2*b*).

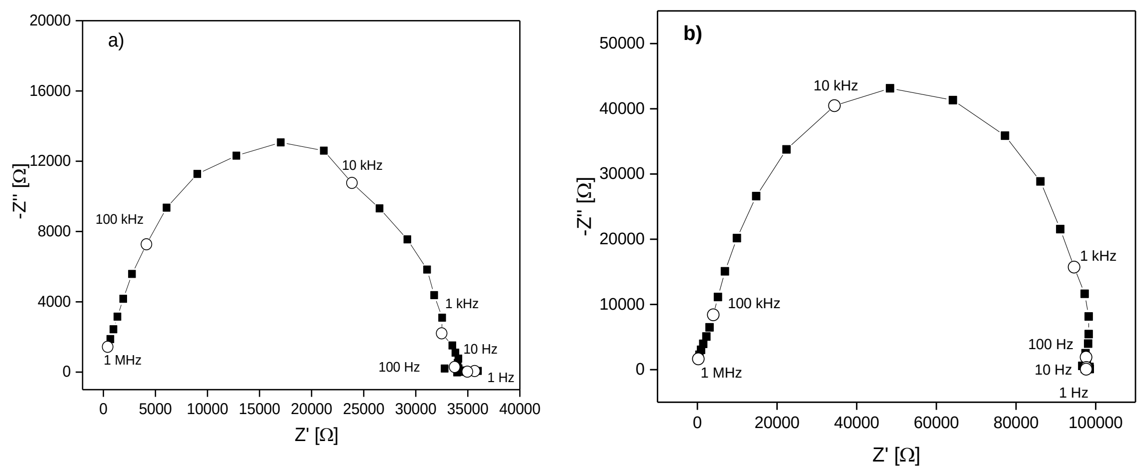


**Fig. 2.** Hodographs of p-Si<Pt> samples before (*a*) and after (*b*) irradiation

The hodograph is described by a similar equivalent electrical circuit and is a regular semicircle. It should be noted that the scatter of points in the LF region is relatively small compared to the unirradiated sample, which indicates a relatively high homogeneity of the conduction channels after irradiation, which is in good agreement with the literature data (Emelyanova *et al*., 2017). The most significant factor of radiation exposure is radiation defects with vacancies. These defects include, first of all, interstitial oxygen $O_i$ – vacancy V (A-center), divacancy (V-V) and the boron complex at the $B_S$ site – vacancy V (E-center).

The presence of platinum in single crystals is confirmed by X-ray spectral microanalysis (Fig. 3), according to which the content of platinum in the samples is 2 at.% or 7 wt.%. The energy dispersive spectra presented in Figure 3a indicate the presence of only platinum in the composition of the studied samples, no other impurity elements were detected.

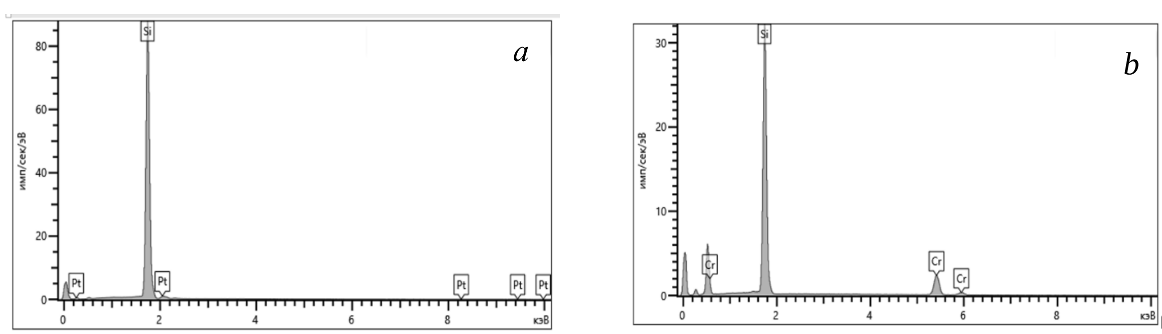


**Fig. 3.** Energy-dispersive spectra of silicon samples; p-Si<Pt> (*a*), p-Si<Cr> (*b*)

The authors of Utamuradova et al. (2021) argue that the presence of a platinum impurity in the silicon lattice slows down radiation defect formation. Moreover, the higher the concentration of platinum, the lower the concentration of radiation defects. Microphotographs of silicon doped with platinum (Fig. 4*b*) indicate the presence of submicron formations in the silicon microstructure, which aggregate into spherical granules after proton irradiation (Fig. 4*c*). According to the energy-dispersive analysis, the detected nanostructures (Fig. 4. *b*,*c*) correspond to the element platinum.

On fig. 5 shows the impedance hodographs of the p-Si sample doped with Cr before and after irradiation. On fig. 5*a*, a semicircle with a limiting ohmic resistance of 65 kΩ is observed. It can be seen (Fig. 5*b*) that after irradiation with protons, the resistance value increases to 79 kΩ.

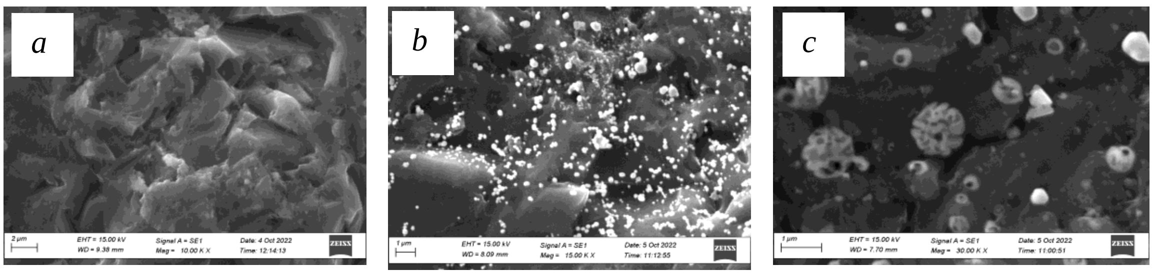


**Fig. 4.** Micrographs of the surface of silicon single crystal wafers before (*a*), after doping with platinum (*b*), and after irradiation with protons (*c*)

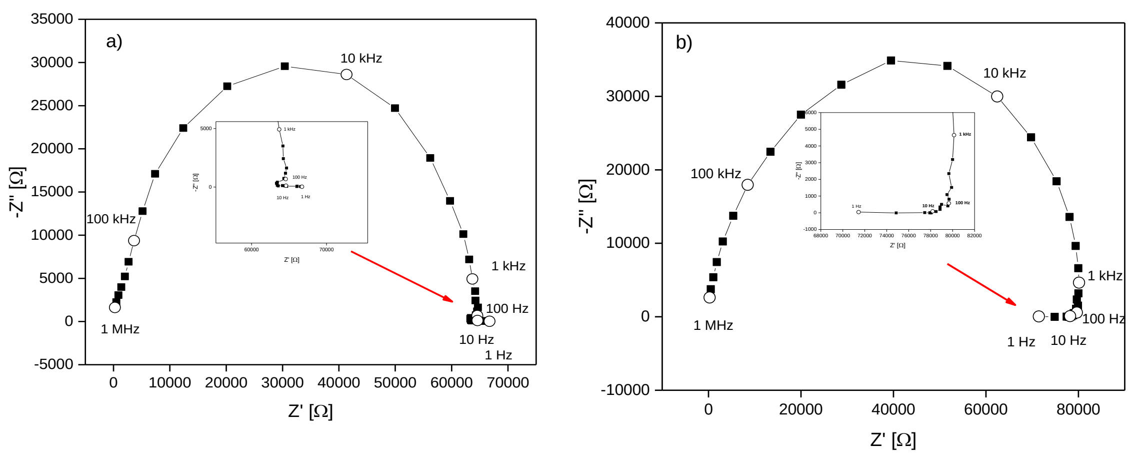


**Fig. 5.** Hodographs of p-Si<Cr> samples before irradiation (*a*), after irradiation (*b*)

The nonlinearity in the frequency range below 100 Hz, corresponding to the uncompensated inductance in p-Si<Cr> material according to (Vladikova *et al*., 2011), can be a manifestation of the formation of linear clusters of radiation defects induced by proton irradiation. The presence of chromium in the studied single crystals in the amount of 19 at.% and 31 wt.% is confirmed by X-ray spectral microanalysis (Utamuradova *et al*., 2022b).

The energy dispersive spectra presented in Figure 3b indicate the presence of only chromium in the composition of the studied samples, and the absence of other impurity elements. On fig. 6 shows typical micrographs of the fracture surface of p-Si single crystals before, after Cr doping, and after proton irradiation. According to fig. 6 *a* and *b*, the morphology of the structural elements of the surface of single crystals did not change significantly after doping with chromium. Interestingly, after irradiation with protons, the morphology of the sample has a columnar microstructure (Fig. 6*c*), which differs significantly from the microstructure of the samples doped with platinum.

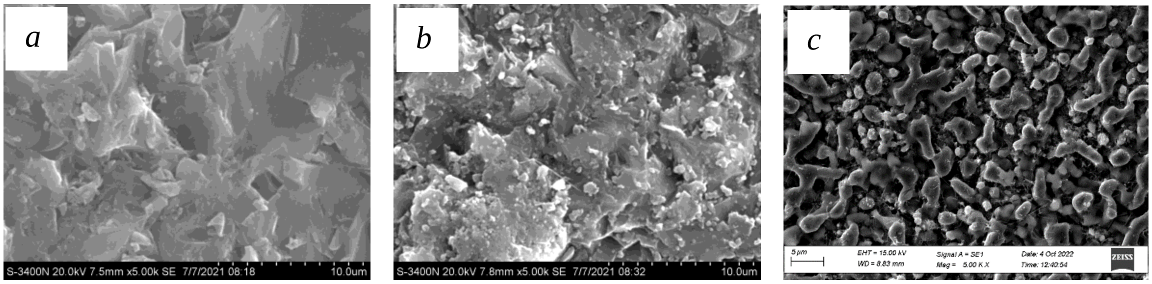


**Fig. 6.** Micrographs of the surface of silicon single crystal wafers before (a), after doping with chromium (b) and after irradiation with protons (c)

## 4. Conclusions

Using electrochemical impedance spectroscopy, it was found that doping p-Si samples with Pt and Cr elements contributes to a significant (3-7 times) increase in their electrical conductivity (Table 1). Irradiation with 2 MeV protons at a dose of $5.1 \times 10^{14}$ particles/cm$^2$ leads to a significant (2-3 times) increase in the electrical resistance of silicon samples, depending on the type of dopant.

**Table 1.** Limit values of ohmic resistance for Si samples doped with Pt and Cr before and after proton irradiation

| | **Resistance (kΩ)** | | |
|---|---|---|---|
| | p-Si | p-Si<Pt> | p-Si<Cr> |
| **Before irradiating** | 222 | 33 | 65 |
| **After irradiating** | 436 | 98 | 79 |

The sample doped with chromium (p-Si<Cr>) has the lowest resistance and the smallest spread of resistances (17%) after irradiation compared to the sample doped with platinum (p-Si<Pt>).

The observed nonlinearity in the frequency range below 100 Hz for the p-Si<Cr> composition may be a consequence of the cluster formation of radiation-induced defects and requires further study.

A radiation-induced change in the microstructure of the surface of silicon crystals doped with chromium has been established, which is probably a consequence of radiation-induced structural self-organization.

**Acknowledgment**

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