

## IR – SPECTROSCOPY OF n-Si<Pt> IRRADIATED WITH PROTONS

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**Abstract.** In this work, the influence of proton irradiation on the concentration of optical active oxygen of silicon samples doped with platinum and the determination of radiation defects that appear after irradiation with protons are studied. For the study, single-crystal n-type silicon samples doped with phosphorus during growth were used. These samples were first doped with platinum, then irradiated with 2 MeV protons at a current of 0.5  $\mu$ A at the EG-5 accelerator. The IR spectra of the samples were obtained using a Shimadzu IRAffinity-1 IR spectrometer.

**Keywords:** Semiconductor, silicon, irradiation, proton, optically active oxygen.

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### 1. Introduction

Today, the world pays great attention to the development of microelectronics and semiconductor materials science. The influence of various types of radiation on semiconductor materials is being intensively studied, the defects created in semiconductors under the action of radiation, as well as their effect on the electrical conductivity of semiconductor materials and structures based on them, are being studied, ways are being sought to eliminate the influence of radiation-induced defects caused by radiation. In this regard, special attention is paid to improving the quality indicators of electronic devices, such as semiconductor electronic devices, solar cells, radiation-sensitive detectors, and increasing the efficiency of long-term operation under radiation exposure (Turgunov *et al.*, 2020; 2021).

At present, the practical use of silicon photoelectronic converters (Si-PEC) in near space conditions is associated with a number of technical difficulties caused by the negative

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impact of external physical factors such as temperature, radiation, and dustiness (Daliev *et al.*, 2015; Kozlov & Kozlovskiy, 2001). The study of the effect of the radiation component, in particular, proton radiation capable of inducing optically active oxygen, on the structure and performance characteristics, in particular, the efficiency of Si-PEC, is an urgent and extremely important scientific task.

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  $\mu\text{m}$  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 (Utamuradova *et al.*, 2022; 2023a).

In order to increase the efficiency of silicon PEC, alloying elements are introduced into the composition of the functional layer. In particular, platinum forms effective recombination centers and can be used to optimize the lifetime of nonequilibrium current carriers in devices (Fistul, 2004). Silicon compensated with platinum has a high photosensitivity in the impurity region of the spectrum.

The aim of this work is to study the effect of radiation to protons on the change in the concentration of optically active oxygen in n-type silicon single crystals doped with platinum (n-Si<Pt>) and to study radiation defect formation after irradiation with hydrogen ions using IR spectroscopy.

## 2. Experimental part

The object under study was n-type silicon (n-Si) with a resistivity of 40  $\Omega\text{ cm}$  grown by the Czochralski method (Milnes A, 1977). The phosphorus dopant concentration in the initial n-Si single crystals was  $7.3 \times 10^{13} - 7.1 \times 10^{15}\text{ cm}^{-3}$ . Doping of silicon with platinum was carried out by the diffusion method with deposition of platinum atoms on the silicon surface in evacuated quartz ampoules at temperatures  $T = 900 - 1250\text{ }^\circ\text{C}$  for 2-10 hours. Subsequent cooling of the samples occurred at different rates (Utamuradova *et al.*, 2021).

The original (n-Si) and doped (n-Si<Pt>) samples after polishing with diamond paste were irradiated with protons with an energy of 2 MeV, at a current of 0.5  $\mu\text{A}$ , using an electrostatic accelerator "EG-5" in the laboratory of neutron physics of the Joint Institute for Nuclear research (FLNP JINR). The dose rate was  $5.1 \times 10^{14}\text{ cm}^{-2}$ .

The concentration of optically active oxygen in silicon samples was determined using an IR spectrometer "Shimadzu IR Affinity-1" in the range of 600-3000  $\text{cm}^{-1}$  in transmission mode. Micrographs of the studied samples were examined using a scanning electron microscope (SEM, Tascan Vega3).

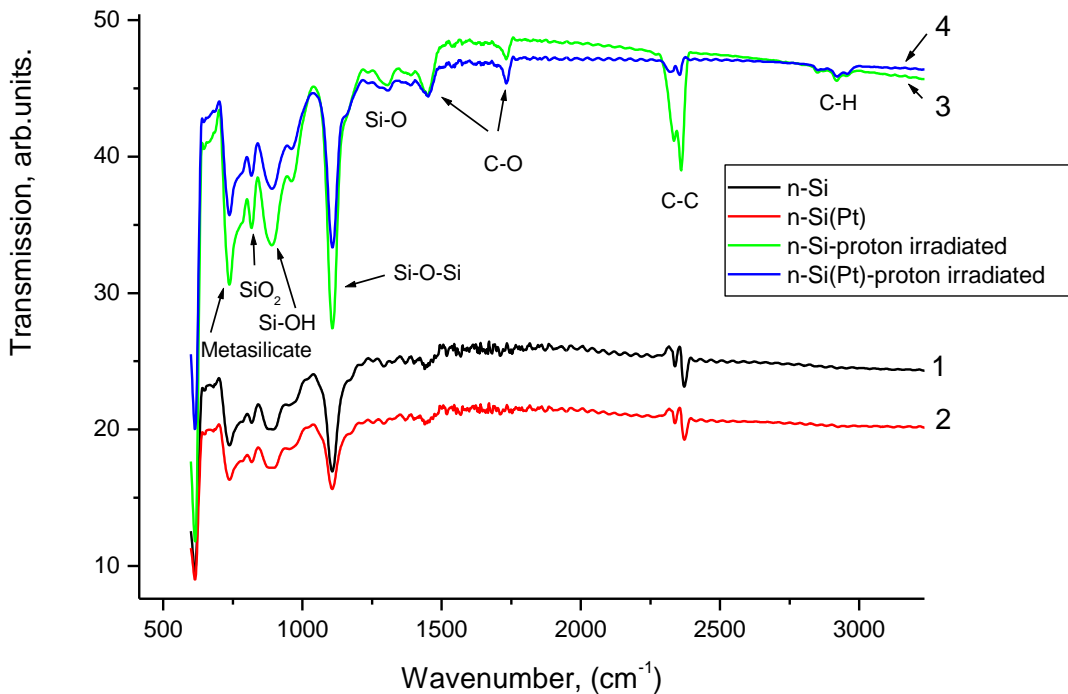
## 3. Results and discussion

Figure 1 shows the IR spectra of single-crystal n-type Si before (curve 1) and after (curve 2) doping with Pt and proton irradiation (curves 3 and 4, respectively). As can be

seen from Fig. 1, in all cases, the IR spectra contain peaks in the region of 1280, 1106, 950, 885, 820 and 740  $\text{cm}^{-1}$ .

According to (Teresa & Choi, 2010), the peaks present in the spectra correspond to different types of chemical bonds: the peak at 1280  $\text{cm}^{-1}$  corresponds to the Si-O bond, the peaks at 1106  $\text{cm}^{-1}$  and 970  $\text{cm}^{-1}$  correspond to the Si-O-Si bonds, the peak at 885  $\text{cm}^{-1}$  corresponds to the Si-OH, peak 820  $\text{cm}^{-1}$  - silica bond  $\text{SiO}_2$  and peak 740  $\text{cm}^{-1}$  - metasilicate bond ( $\text{SiO}_3$ ). The peak at the wave number 2360  $\text{cm}^{-1}$  corresponds to the C-C bond (Feifel & Lisdat, 2011).

When silicon is doped with platinum, the intensity of the peaks in the infrared transmission mode changes most significantly only in the band corresponding to the wave number 1106  $\text{cm}^{-1}$ , the intensity of the other peaks remains practically unchanged.



**Fig.1.** IR spectra of single-crystal n-type Si before (curve 1) and after (curve 2) Pt doping and proton irradiation (curves 3 and 4, respectively)

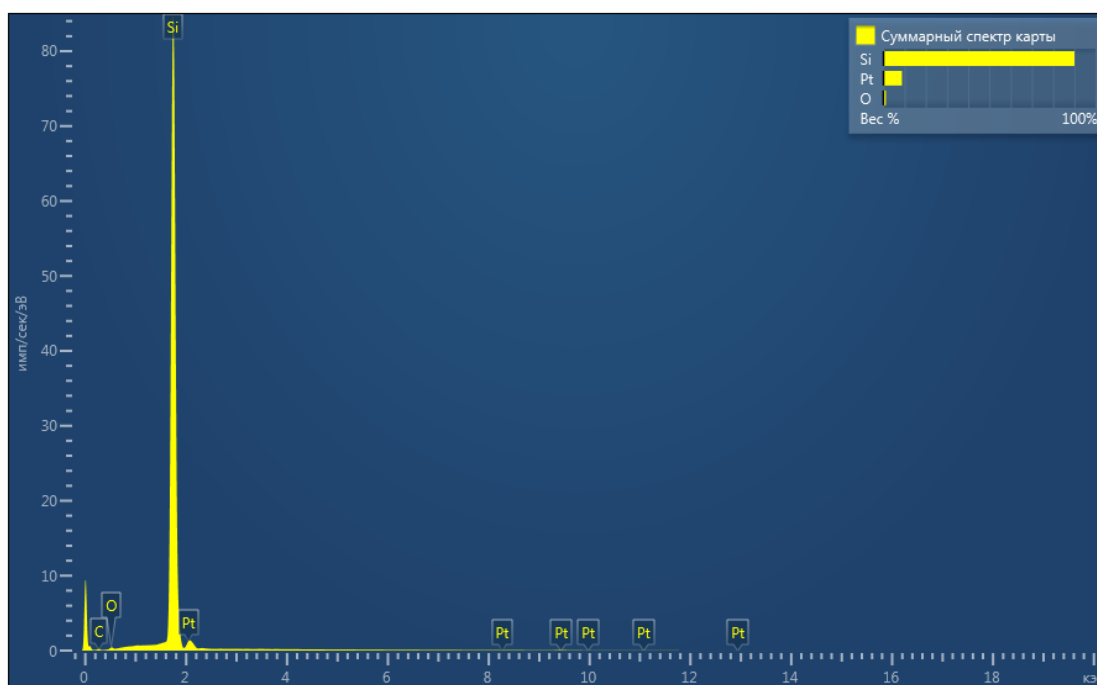
According to (Kissinger, 2019), oxygen can be present in single-crystal silicon both in the atomically dispersed state and in the form of defective complexes. In the dispersed state, oxygen is in the interstitial position, forming a Si-O-Si quasi-molecule with two neighboring silicon atoms. In this case, the oxygen atoms that make up the Si-O-Si quasi-molecule are optically active and have a number of natural vibrational modes: 1225, 1106, 515  $\text{cm}^{-1}$  (at  $T = 300$  K). As the temperature decreases, these bands shift, split, and change in intensity. The most intense IR absorption band is the band at 1106  $\text{cm}^{-1}$  (9.1  $\mu\text{m}$ ), therefore, in practice, this band is used to determine the atomic oxygen content in the crystal. The concentration of optically active oxygen ( $N_{\text{O}}^{\text{opt}}$ ) is proportional to the absorption coefficient  $\alpha_{\text{max}}$  at the maximum of the 1106  $\text{cm}^{-1}$  band:

$$N_{O}^{Opt} = K \cdot \alpha_{max}, \quad (1)$$

where  $K$  is the coefficient of proportionality.

Comparison of the IR absorption spectra of the control and doped samples shows that the introduction of platinum atoms through diffusion leads to a significant decrease (2 times in some samples) in the oxygen concentration. This effect is probably due to the interaction of platinum and oxygen atoms in silicon and confirms the data of various authors on the aggregation of impurity atoms with oxygen (Utamuradova & Rakhmanov, 2022; Golosov *et al.*, 2019).

The presence of platinum in single crystals is confirmed by X-ray spectral microanalysis, according to which the content of platinum in the samples is 2 at.% or 12 wt.%. The energy dispersive spectra (Fig. 2) indicate the presence in the composition of the studied samples, in addition to platinum atoms, of oxygen and carbon atoms. The content of oxygen atoms in the samples is 0.85 at.% or 1.2 wt.%, carbon atoms 0.7 at.%, respectively.

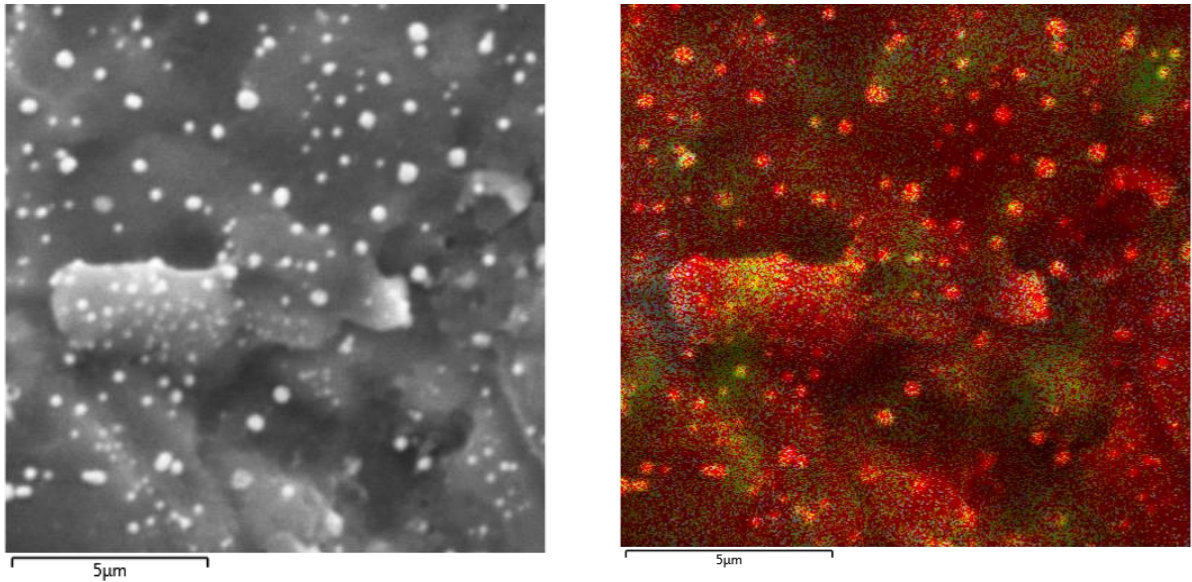


**Fig.2.** Energy-dispersive spectra of silicon samples doped with platinum

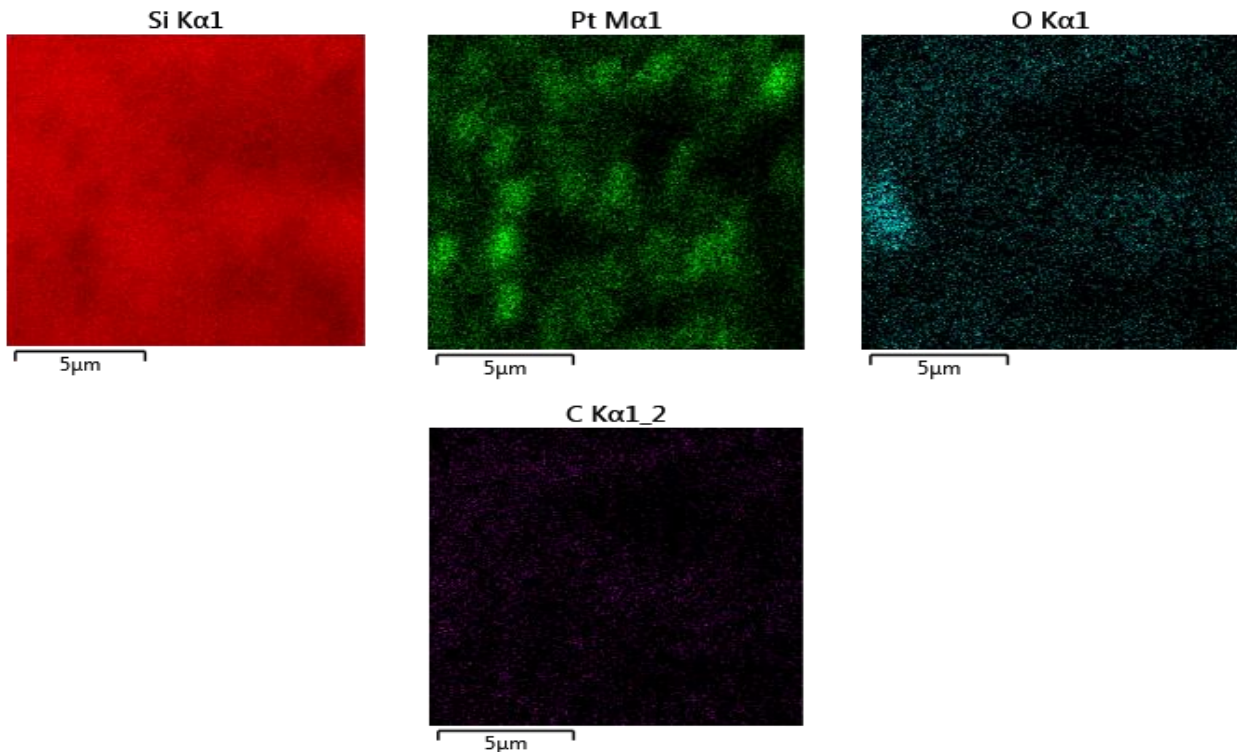
Micrographs from the surface of silicon samples doped with platinum show the presence of nanosized inclusions of a spherical shape (Fig. 3). According to the maps of the distribution of elements over the surface presented in Figure 4, the detected nanosized inclusions consist of platinum, oxygen, and carbon, with oxygen and carbon atoms distributed relatively evenly in silicon (Fig. 4). Therefore, aggregation of the Pt impurity by diffusion takes place.

Irradiation of the original and doped samples with protons leads to an increase in the intensity of the peaks at  $1106 \text{ cm}^{-1}$  and  $885 \text{ cm}^{-1}$ . A comparison of the IR absorption spectra of unirradiated and irradiated n-Si<Pt> samples shows that the implantation of hydrogen

ions in silicon after irradiation leads to a significant increase in the concentration of optically active oxygen  $\text{No}^{\text{opt}}$ . New peaks appear on the IR spectra of the irradiated samples at  $1450\text{ cm}^{-1}$ ,  $1730\text{ cm}^{-1}$  and  $2912\text{ cm}^{-1}$  (Fig.1), corresponding to the C-O bonds ( $1450\text{ cm}^{-1}$ ,  $1730\text{ cm}^{-1}$ ) and C- H ( $2912\text{ cm}^{-1}$ ) ( Feifel & Lisdat, 2011).



**Fig. 3.** Electronic image and multilayer EMF map n-Si<Pt>



**Fig.4.** Micrographs of the surface of a single crystal of silicon after doping with platinum with maps of the distribution of elements



The main and most significant changes in the properties of proton-irradiated silicon are radiation defects, the structure of which includes vacancies. These radiation defects include, first of all, the complex interstitial oxygen  $O_i - V$  vacancy (A-center), Divacancy (V-V) and the phosphorus complex at the  $P_S$  site – vacancy (E-center) (Utamuradova *et al.*, 2023b). In irradiated silicon with a high concentration of oxygen and carbon, the K center is more thermally stable than the E center. This point radiation defect is a complex consisting of an interstitial oxygen atom and an interstitial carbon atom ( $O_i - C_i$ ) (Paulescu *et al.*, 2019). The K-center corresponds to the donor level  $E_V + 0.36$  eV near the bottom of the silicon band gap, which has a relatively large charge carrier capture cross section.

Relatively close to the A center in the band gap of silicon is the level of the radiation defect, which is a complex of the interstitial carbon atom  $C_i$  and the carbon atom at the  $C_S$  site. This radiation defect is usually observed in crystals with a relatively low dissolved oxygen concentration and a high  $C_S$  concentration, when the  $C_S$  carbon atoms themselves become the main traps for  $C_i$  atoms. Similar effects with the parameters of the  $C_i - C_S$  center are exhibited by the  $C_i - Si - C_S$  defects observed in silicon irradiated with protons (Asadchikov *et al.*, 2019).

Based on (Utamuradova *et al.*, 2023b; Paulescu *et al.*, 2019; Asadchikov *et al.*, 2019), it can be assumed that the irradiation of n-Si and n-Si<Pt> samples with protons, synthesized in this work by protons with an energy of 2 MeV with a dose rate of  $5.1 \times 10^{14}$   $\text{cm}^{-2}$ , leads to the formation of radiation defects of the type  $O_i - C_i$ ,  $C_i - C_S$ . Radiation defects characteristic of silicon (proton irradiation) such as the A-center, divacancies, and E-centers could not be explicitly detected by IR spectroscopy.

The appearance of new hydrocarbon (C-H) bonds in silicon ( $2912 \text{ cm}^{-1}$ , Fig. 1) after irradiation with protons is presumably due to the interaction of implanted hydrogen ions with the technological impurity of carbon. Irradiation with protons also leads to an increase in the concentration of Si-OH and C-C bonds due to an increase in the concentration of hydrogen in silicon during irradiation. Doping of silicon with platinum reduces the concentration of Si-OH and C-C bonds due to the strong bond of platinum atoms with technological impurities (O and C) (Elsad *et al.*, 2023; Utamuradova *et al.*, 2023<sup>a</sup>).

#### 4. Conclusions

When silicon is doped, Pt atoms react with technological impurities to form complexes of the (Pt-O) type, as a result of which the concentration of interstitial optically active oxygen  $N_{O}^{\text{opt}}$  decreases. Irradiation of single-crystal silicon n-Si and n-Si<Pt> wafers with hydrogen ions ( $F = 5.1 \times 10^{14} \text{ cm}^{-2}$ ) breaks the resulting Pt-O bonds formed after doping, which leads to an increase in the concentration of optically active oxygen ( $N_{O}^{\text{opt}}$ ) at 25-30% of its initial concentration, which probably leads to a decrease in the efficiency of silicon materials.

Irradiation with protons leads to the creation of radiation defects of the  $O_i - C_i$  and  $C_i - C_S$  types in silicon, the formation of a C-H bond and an increase in the concentration of the Si-OH bond. By doping with platinum atoms, we can increase the radiation resistance of silicon (slow down radiation defect formation) and reduce the concentration of the Si-OH bond.

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