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STUDYING THE INFLUENCE OF PROTON IRRADIATION ON THE DISTRIBUTION PROFILE OF Pt AND Cr IN SURFACE LAYERS n-Si<Pt>, n-Si<Cr> USING ELLIPSOMETRIC SPECTROSCOPY

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Abstract. In this work, the effect of high-temperature doping and proton irradiation on the depth profile and the creation of layers on the surface of single-crystal silicon was studied. The study used single-crystal n-type silicon samples doped with phosphorus during growth. These samples were first doped with platinum and chromium and after polishing they were irradiated with protons with an energy of 2 MeV, a dose of 5.1×10^{14} cm^{-2} at the EG-5 accelerator. Studies of the optical properties of the sample surface were carried out using an ELLIPS-1991 spectroscopic ellipsometer at room temperature.

Keywords: *Silicon, platinum, chromium, doping, proton irradiation, ellipsometric spectroscopy.*

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1. Introduction

The dominant impurities in solar grade silicon are known to be phosphorus and oxygen. A large number of works are devoted to the study of the properties of these impurities and the reactions occurring with their participation in silicon. However, many questions related to the identification of defects that contain these impurities still remain speculative. Thus, quite a large number of works are devoted to the study of a defect that occurs in solar PV cells in the first hours of their operation and leads to a loss of 10% of their efficiency (Madatov *et al.*, 2024; Bogatov *et al.*, 2019; Utamuradova *et al.*, 2023c).

Technologies for proton irradiation of semiconductors and semiconductor devices make it possible to selectively change their mechanical, optical, electrical and recombination characteristics (Kozlov & Kozlovskiy, 2001; Turgunov *et al.*, 2023). The

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damaged layer formed as a result of implantation of hydrogen ions is inhomogeneous; studying its properties is an urgent problem in semiconductor physics (Utamuradova *et al*., 2023a).

Currently, the practical use of silicon photoelectronic converters in near space conditions is associated with a number of technical difficulties due to the negative impact of external physical factors such as temperature, radiation and dust (Ahmadova & Jabarov, 2023; Komarov *et al*., 2013). Studying the effect of the radiation component, in particular proton radiation, which can change the surface layers, on the structure and operational characteristics, in particular, the efficiency of Si-PV, is a current and extremely important scientific task.

The purpose of this work is to study the effect of diffusion doping and proton irradiation on the formation of surface layers of silicon single crystals using ellipsometric spectroscopy.

2. Experimental part

The objects under study were n-type silicon wafers measuring 1.5 x 6 x 13 mm^3 with a resistivity of 40 Ohm cm (grade KEF-40). The wafers were cut from silicon ingots grown by the Czochralski method. The concentration of phosphorus dopant in the initial n-Si samples was 4.2×10^{14} at/cm^3. Diffusion doping of silicon with platinum and chromium was carried out from a layer of metal Pt and Cr deposited on the silicon surface in evacuated quartz ampoules at temperatures of 1200 °C for 2 hours. Subsequent cooling of the samples was carried out using the thermal regimes given in (Azamatov *et al*., 2023; Turgunov *et al*., 2021).

After thorough cleaning and polishing of the surface, the doped samples were irradiated with protons with an energy of 2 MeV, at a current of 0.5 μA to obtain a dose of 5.1×10^{14} cm^{-2} using the electrostatic accelerator “EG-5” in the Laboratory of Neutron Physics of the United Institute for Nuclear Research (FLNP JINR).

Studies of the optical properties of the sample surface were carried out using an ELLIPS-1991 spectroscopic ellipsometer at room temperature. The measurements were carried out in the wavelength range 350 ÷ 1000 nm with a step of 2 nm, the angle of incidence of the light beam was 70°. To determine the elemental composition of silicon samples, the method of X-ray spectral microanalysis using a scanning electron microscope (SEM) was used.

3. Results and their discussion

In this work, experiments were carried out using ellipsometric spectroscopy and the optical parameters of various layers formed on the surface of doped samples were determined. Figure 1 shows the Ψ- and Δ-spectra of the original and doped samples with platinum and chromium.

Ellipsometry measures the change in polarization as light is reflected or transmitted from a material structure. The change in polarization is represented as the amplitude ratio Ψ and the phase difference Δ. The measured response depends on the optical properties and thickness of the individual materials.

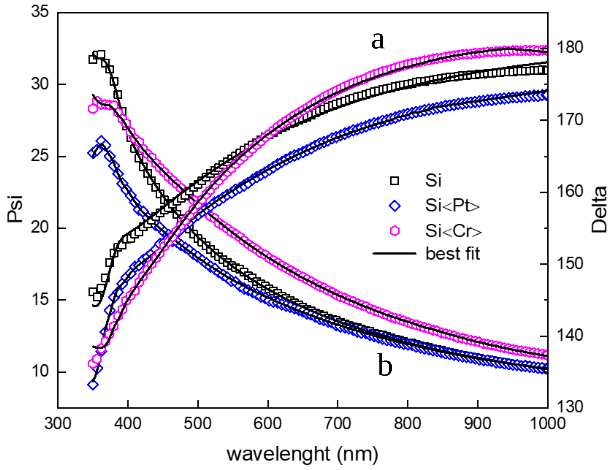

Figure 1. Ψ spectra (a) and Δ spectra (b) of samples: black curve - original, blue curve - doped with platinum and pink curve - doped with chromium. The black line is the best fit curve

Using ellipsometry, oxide layers with a thickness of 5.377 nm were discovered on the surface of the original sample using software "V.A.S.E" for ES. After doping with platinum and chromium, oxide layers with a thickness of 8.979 and 17.24 nm, respectively, were determined (Table 1). In addition to the oxide layers, near-surface layers with a thickness of 30.4 and 56.5 nm were also discovered. A layer of natural oxide formed and developed on the surface of the samples. This can happen for a variety of reasons, including the roughness of the sample, the temperature of the alloying treatment and the time the sample is exposed to air.

Table 1. Parameters of oxide and subsurface layers on the surface of silicon samples

No	Samples	Thickness (nm)	
		Native oxide layer	Subsurface layer
1	Si	5.377	0
2	Si-Pt	8.979	30.4
3	Si-Cr	17.24	56.5

It is known that a natural oxide layer is formed on the surface of semiconductor materials in an oxygen atmosphere (Daliev & Saparov, 2023). Therefore, in the three-layer model used to explain the results of ellipsometric spectroscopy measurements, the natural oxide layer is always taken into account. After alloying, surface layers appear due to thermal diffusion, which is used for alloying with platinum and chromium. The authors (Tsang *et al.*, 1984) determined the formation of PtSi on the surface of n-Si<Pt>. Multichannel Raman spectroscopy was used to quantitatively characterize the formation of PtSi at the platinum-Si(100) interface, where spectra were obtained from PtSi layers up to 10 Å thick and from <40 Å PtSi at 140 Å from Pt. Other authors (Utamuradova *et al.*, 2023b) have also identified silicides in n-Si<Cr> as vibrations associated with the $CrSi_2$ compound using Raman spectroscopy. Based on (Tsang *et al.*, 1984; Utamuradova *et al.*, 2023b), we assume that the subsurface layer that is created after diffusion belongs to platinum and chromium silicides.

The calculations used a three-layer model, including a natural oxide layer, a near-surface layer and a crystalline silicon substrate (Utamuradova *et al.*, 2023d). For the natural oxide layer, the Cauchy and Urbach dispersion model was used (Figure 2) and for the near-surface layer of the samples, the Si parametric model was used (Figure 3).

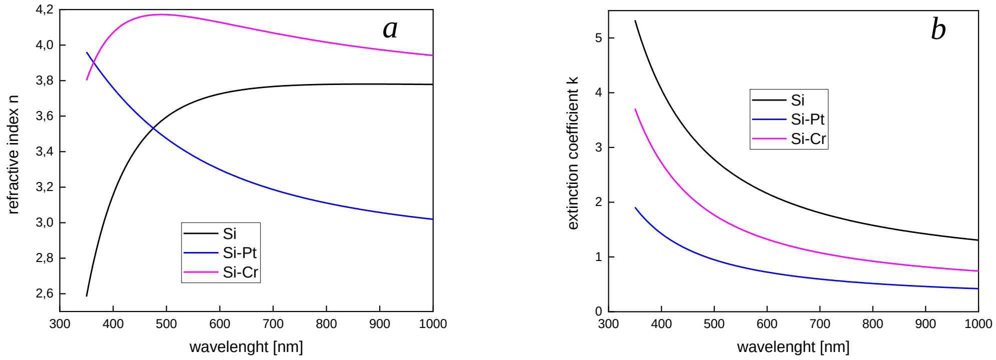

Figure 2. Optical constant spectra of Cauchy and Urbach: a - refractive index n(λ); b - extinction coefficient k(λ)

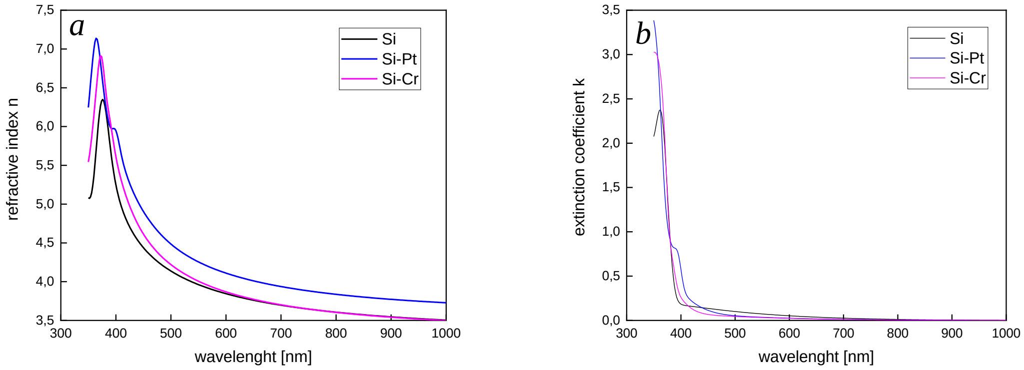

Figure 3. Optical constant spectra for the surface layer of Si samples. a - refractive index n(λ); b - extinction coefficient k(λ)

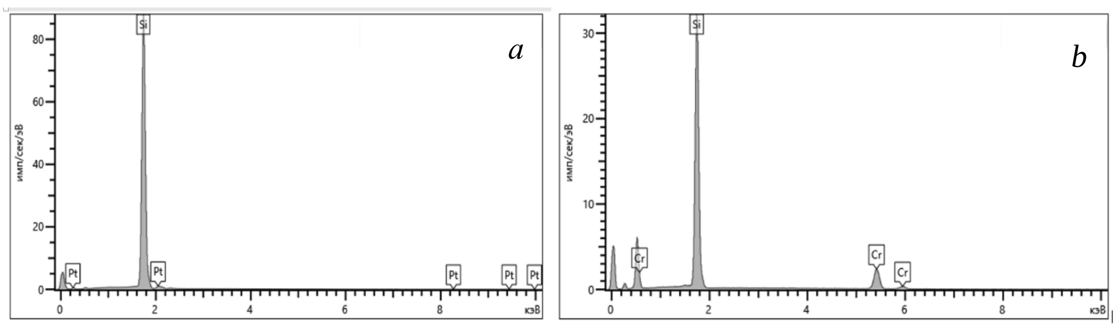

Figure 4. Energy dispersive spectra of silicon samples: a) n-Si<Pt>, b) n-Si<Cr

The presence of platinum in single crystals is confirmed by X-ray spectral analysis (Figure 4), according to which the platinum content in the samples is 3 at.% or 9 wt.%. The energy-dispersive spectra presented in Figure 4a indicate the presence of only platinum in the composition of the samples under study; no other impurity elements were detected. The presence of chromium in the studied single crystals in an amount of 12 at.% and 25 wt.% is confirmed by X-ray spectral analysis. The energy-dispersive spectra presented in Figure 4b indicate the presence of only chromium in the composition of the samples under study and the absence of other impurity elements.

Next, we irradiated these samples with protons with an energy of 2 MeV at a current of 2 μA. Figure 5 shows the Ψ- and Δ-spectra of proton-irradiated samples. These spectra show that after proton irradiation, the thickness of the oxide and near-surface layers decreases on the surface of doped silicon samples (Table 2).

Table 2. Parameters of oxide and near-surface layers on the surface of irradiated silicon samples

No	Samples after irradiation	thickness (nm)	
		native oxide layer	subsurface layer
1	Si-Pt	5.4947	3.7997
2	Si-Cr	11.891	14.084

If we compare individually, the oxide layers in n-Si<Pt> after irradiation with protons decrease from 8.979 nm to 5.4947 nm. The surface layers also decrease from 30.4 nm to 3.7997 nm. In samples doped with chromium, such effects were also observed: the oxide layers in n-Si<Cr> after irradiation with protons decrease from 17.24 to 11.891 nm and the subsurface layers from 56.5 nm to 14.084 nm.

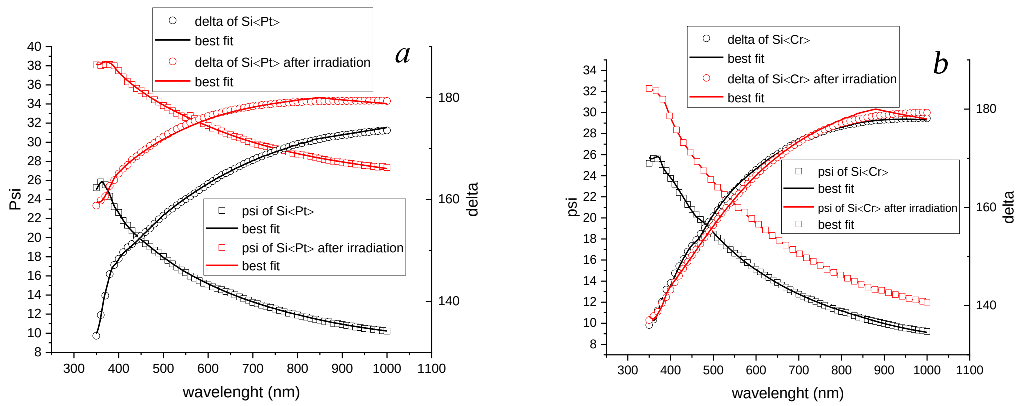

Figure 5. Ψ spectra and Δ spectra of irradiated silicon samples: a-doped with platinum and b - doped with chromium. The black and red line is the best fit curve

The authors (Utamuradova *et al*., 2023e) in their work studied the effect of proton irradiation on the structure of silicon samples and they found that proton irradiation leads to disruption of the crystal structure on the surface of silicon samples. Other authors (Doyama *et al*., 1992) determined that proton irradiation leads to amorphization of silicon samples.

Based on (Doyama *et al*., 1992), it can be assumed that irradiation with protons leads to a decrease in the oxide and subsurface layers on the surface of doped samples due to disruption of the structure and amorphization, which changes the crystalline structure of single-crystal silicon.

The Cauchy and Urbach dispersion models give the following dependence of the refractive index n(λ) and extinction coefficient k(λ) on the light wavelength λ(nm), respectively (Utamuradova *et al*., 2023b):

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots \quad (1)$$

$$k(\lambda) = \alpha e^{\beta\left(1240\left(\frac{1}{\lambda} - \frac{1}{\gamma}\right)\right)} \quad (2)$$

where A, B, C are the Cauchy coefficients, α is the amplitude of the extinction coefficient, β is the exponential factor, γ is the edge of the band.

Also, Figure 6 shows the Cauchy and Urbach dispersion model for determining the oxide layer and Figure 7 shows the parametric model for determining the diffusion layer on the surface of irradiated samples.

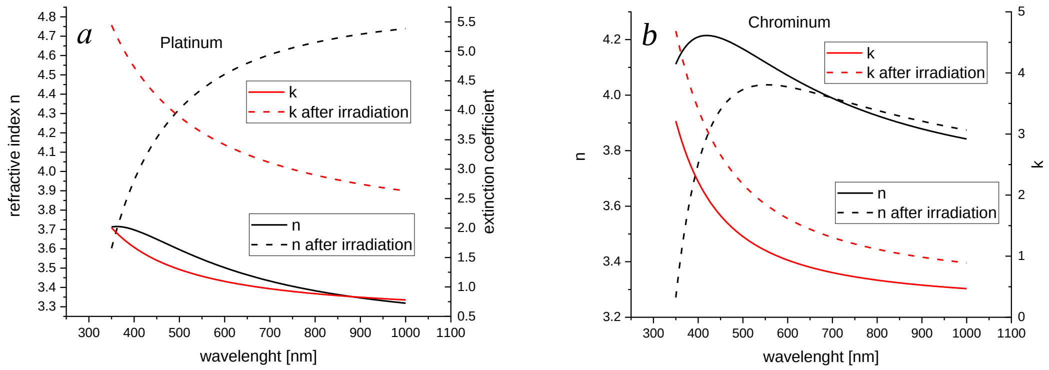

Figure 6. Optical constant spectra of Cauchy and Urbach for irradiated samples: a - refractive index n(λ); b - extinction coefficient k(λ)

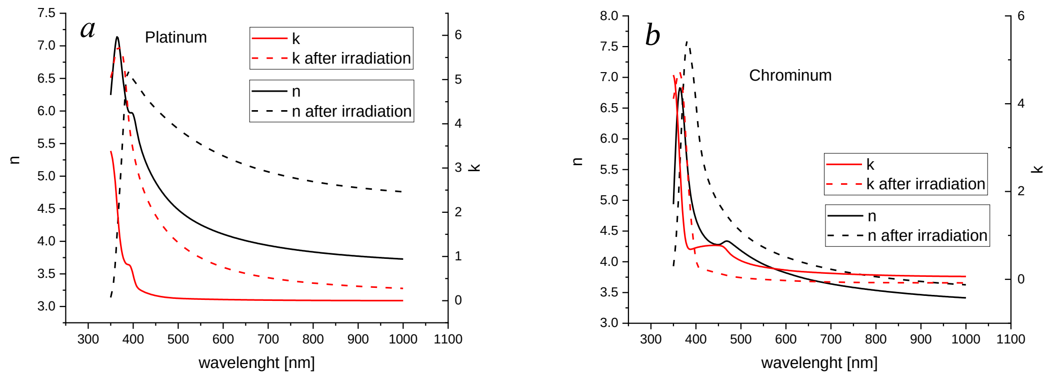

Figure 7. Optical constant spectra for the subsurface layer of irradiated Si samples. a - refractive index n(λ); b - extinction coefficient k(λ)

4. Conclusion

Using ellipsometric spectroscopy, the presence of near-surface and oxide layers on the surface of the original, doped and irradiated samples was established. It was found that in the initial samples only an oxide layer with a thickness of 5.377 nm appears. After alloying with platinum and chromium, in addition to the oxide layer, near-surface layers also appear. The thickness of the surface layers in silicon doped with chromium is almost 2 times greater than in silicon samples doped with platinum.

Further irradiation with protons with an energy of 2 MeV, a dose of 5.1×10^{14} cm^{-2}, leads to a decrease in the oxide and subsurface layers on the surface of silicon samples. We assume that this happens due to a disruption in the crystal structure of these samples.

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