DOI 10.31489/2023No3/35-42

UDC 539.3/.6; 621.315.592

PROCESSES OF DEFECT FORMATION IN SILICON DIFFUSIONALLY DOPED WITH PLATINUM AND IRRADIATED WITH PROTONS

Utamuradova Sh.B. [1], Daliev Sh.Kh.[1], Rakhmanov D.A.[1*], Doroshkevich A.S.[2], Genov I.G.[2,3], Tuan P.L.[2,4], Kirillov A.K.[2]

[1] Institute of Semiconductor Physics and Microelectronics, National University of Uzbekistan named after Mirzo Ulugbek, Tashkent, Uzbekistan, dilmurod-1991@bk.ru
[2] Joint Institute for Nuclear Research, Dubna, Russia
[3] Institute of Electrochemistry and Energy Systems "Acad. Evgeni Budevski"- Bulgarian Academy of Sciences, Sofia, Bulgaria
[4] Hanoi Irradiation Center, Vietnam Atomic Energy Institute, Hanoi, Vietnam

In this work, we studied the effect of technological regimes and proton implantation on the processes of defect formation in single-crystal n-type silicon (n-Si) doped with platinum using the method of impedance spectroscopy. It has been established that radiation-induced changes in the electrical conductivity of silicon depend significantly on the technological regimes of doping with impurities in silicon. Hodographs show that doping with platinum leads to a decrease in the electrical resistance of silicon samples. Irradiation with 2 MeV protons at a dose of 5.1 × 10^{14} particles / cm^2 leads to a significant (2-3 times) increase in the electrical resistance of the silicon samples under study. It is concluded that the relatively high resistance to radiation exposure (resistance change of no more than 16%: from 55 kΩ to 65 kΩ as a result of ion implantation) of samples doped at 1200°C is presumably due to a higher concentration of impurity ions (platinum) in the samples volume compared to 1100°C.

Keywords: silicon, platinum, doping, high-temperature diffusion, proton irradiation.

1. Introduction

Modeling, synthesis and research of new functional materials are among the most urgent scientific problems of our time. The microstructure and isovalent impurities determine the functional properties of materials of this class. That is why the study of the electrical properties of semiconductors and semiconductor structures, taking into account their real microstructure, is an important and urgent task [1-4]. New materials based on silicon, in particular, those containing platinum (n-Si<Pt>) as a dopant (n-type conductivity), have not been studied enough and are of interest for fundamental science and practical applications.

Modification of the properties 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 [5,6]. Interest in the implantation of protons in silicon crystals 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 the accumulation of hydrogen atoms [7,8].

The purpose of this work is to study the effect of technological regimes and proton implantation on the processes of defect formation in single-crystal n-Si<Pt> using impedance spectroscopy.

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. 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 [9].

.

2. Materials and methods

The objects under study were n-type silicon wafers 1.5 x 6 x 13 mm in size with a resistivity of 40 Ω cm (KEF-40 grade). The wafers were cut from silicon ingots grown by the Czochralski method. Diffusion doping of silicon with platinum was carried out from a layer of metallic Pt deposited on the silicon surface in evacuated quartz ampoules at temperatures of 1100 and 1200 °C for 2 hours. Subsequent cooling of the samples was carried out using the thermal regimes given in [10–12]. The phosphorus dopant concentration in the initial n-Si samples was 4.2×10^{14} at/cm^3.

After thorough cleaning 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} particles / cm^2 using an electrostatic accelerator "EG-5" in the Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (FLNP JINR).

The study of the EIS of silicon samples was carried out at room temperature (300°K) on an impedancemeter "Sp-200 BioLogic" in the frequency range of 1 Hz ÷ 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. In our representation of a contour with distributed parameters, these parameters were calculated according to the expression:

$$\tau_f = R_1P_1,\ \tau_d = (R_1)^2/(2W_{sr1}^2) \quad (1)$$

The optical properties of the surface of the samples were studied 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°. The elemental composition of silicon samples was determined by X-ray spectral microanalysis using a scanning electron microscope (SEM).

3. Results and discussion

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

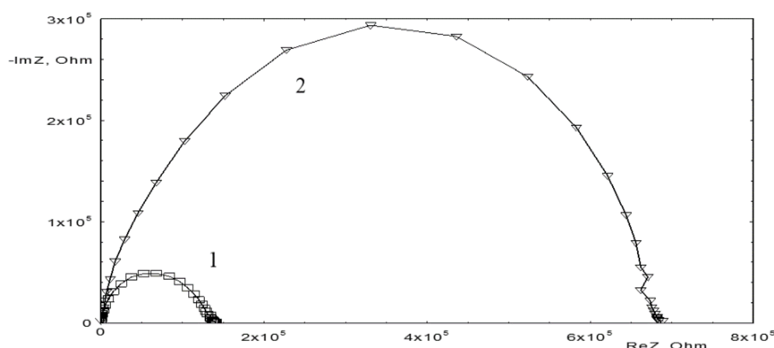


Fig.1. Hodographs of the original n-Si sample. before (1) and after (2) irradiation.

The impedance spectrum (Fig. 1, 1-curve) is in the resistance range 93Ω÷ 128.7 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 ÷ 93 Ω along the X axis corresponds to the resistance of the electrolyte [13,14].

The impedance spectrum of the irradiated sample (Fig. 1, curve 2) has a similar shape and is in the range 248 Ω ÷ 673 kΩ. It can be seen that irradiation in this case led to an increase (by almost a factor of 5) in the resistance of the sample, presumably due to the formation of defects in the crystal lattice [15,16].

On figure 2 shows the impedance curves of the n-Si samples doped with Pt at a temperature of 1100°C for 2 hours before and after irradiation. A curve in the form of an arc of a circle is observed in the range of ohmic resistance values up to 99.42 kΩ. Irradiation leads to an increase in ohmic resistance at least 4 times (up to 422 kΩ, Fig. 2. 2-curve).

The hodograph of fig.2, as in the case of fig.1, can be described by one equivalent electrical circuit (fig.3). It should be noted that the scatter of points in the low-frequency 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 [17]. The most significant factor of radiation exposure is radiation defect formation, in particular, the formation of vacancies. Among such defects, one should first of all include oxygen vacancies Oi - vacancy V (A-center), divacancies (V-V) and the boron complex P_S (at the site) - vacancy V (E-center).

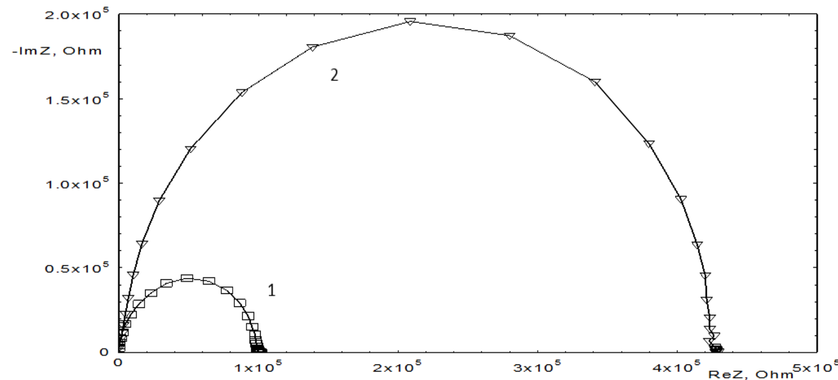


Fig. 2. Hodographs of the I-batch of n-Si samples doped with Pt before (1) and after (2) irradiation. T_{diff}=1100 °C, t_{diff} =2 hours.

Fig.3. Equivalent electrical circuit, where R_1 is active resistance; CPE - constant phase element; Ws_1 is the “final” Warburg element characterizing the diffusion properties of the sample.

On figure 4 shows the impedance hodographs of the n-Si sample doped with platinum (t_{diff} = 2 h, T_{diff} = 1200°C) before and after irradiation. On fig. 4 (curve 1) there is a semicircle with a limiting ohmic resistance of 55 kΩ. Consequently, doping led to a decrease in the ohmic resistance of the sample by almost 2 times. It can be seen (Fig. 4, curve 2) that irradiation with protons leads to an increase in the resistance value from 55 kΩ to 65 kΩ.

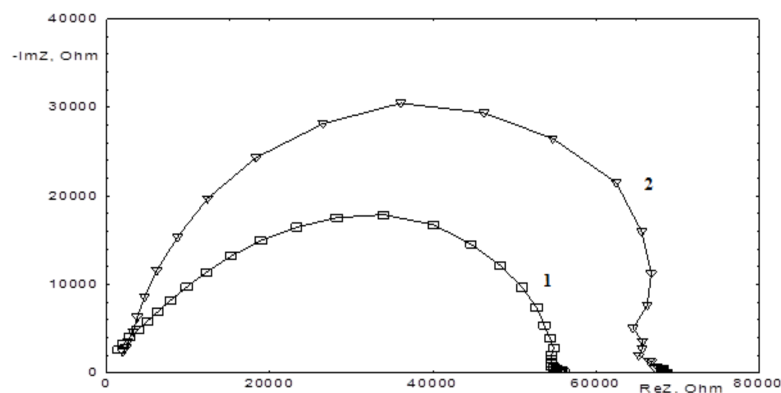


Fig. 4. Hodographs II - batch of samples of n-Si doped with Pt before (1) and after (2) irradiation. T_{diff}=1200°C, t_{diff}. =2 hours.

Analysis of the obtained results showed that the slope of the hodograph (Fig. 4, curve 1) of the unirradiated sample at high frequencies is 39°, i.e. a linear diffusion process occurs in a homogeneous layer with a slight deviation from Fick's second law [18]. After irradiation of the samples (Fig. 4, 2-line), the slope increases to 65.45°, i.e. diffusion limitations appear, which are probably associated with a violation of the homogeneity of the material. The obtained results showed that irradiation of n-Si<Pt> samples by protons with an energy of 2 MeV with a dose of 5.1×10^{14} particles / cm^2 leads to a significant increase (2-3 times) in the electrical resistance of the silicon samples under study. Moreover, the observed effect largely depends on the doping temperature (Table 1).

.

Table 1. Limiting values of ohmic resistance of Si samples doped with Pt at 1100°C and 1200°C before and after proton irradiation.

	Sample resistance [kΩ]		
	n-Si	n-Si<Pt> 1100 °C	n-Si<Pt> 1200 °C
Before irradiation	129	99	55
After irradiation	673	422	65

The results of measurements of the impedance of the studied samples showed that there is a linear decrease in electrical resistance, starting from a frequency of 1000 Hz. Up to a frequency of 1000 Hz, the electrical resistance remains almost unchanged. Table 2 below shows the values of the active resistance of the equivalent circuit described by the Rendlis circuit [19]. These values also undergo changes after doping and irradiation, in particular, after doping - decreases, after irradiation - increases (Table 2).

The frequency dependence of the Randlis contour can be expressed in terms of two time constants for the Faraday (τ_f) and diffusion (τ_d) processes [19]:

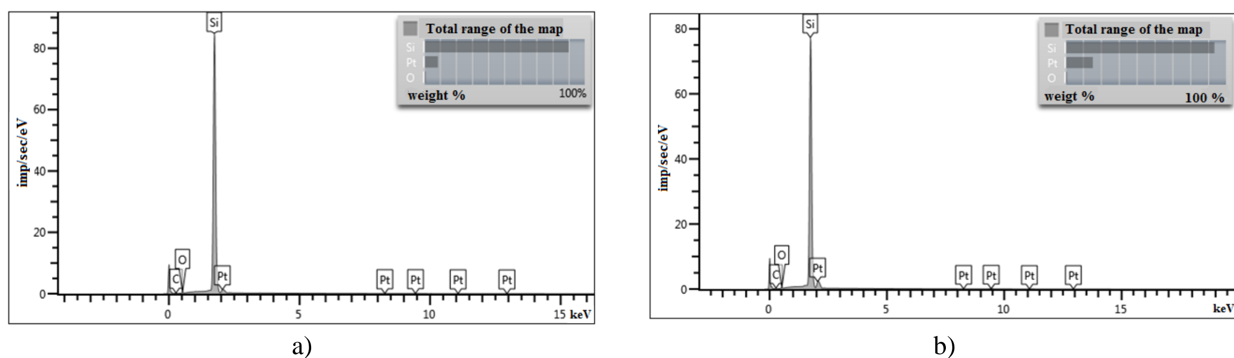
$$\tau_f = R_{ct}C_{dl}\ ,\ \tau_d = (R_{ct})^2/(2W_{sr}^2) \quad (2)$$

The relatively high resistance to radiation exposure (resistance change of no more than 16%: from 55 kΩ to 65 kΩ as a result of ion implantation) of samples doped at 1200°C is presumably due to a higher concentration of impurity ions (platinum) in the sample volume compared to 1100°C (the coefficient of diffusion of platinum at 1200°C is almost 3 times higher than at 1100°C) [20,21].

Table 2. Summary table for the variant of EEC approximation by the Randlis contour with distributed parameters.

Options	n-Si	n-Si (irradiated)	n-Si<Pt> (1100 ^{0}C)	n-Si<Pt> (1100 ^{0}C, irradiated)	n-Si<Pt> (1200 ^{0}C)	n-Si<Pt> (1200 ^{0}C, irradiated)
R_1	1.0414×10^5	4.6704×10^5	98320	4.3122×10^5	22513	25789
P_1	2.8859×10^{-10}	4.6399×10^{-10}	1.4253×10^{-10}	1.9715×10^{-10}	4.143×10^{-09}	3.7722×10^{-10}
n_1	0.9345	0.88054	0.94156	0.91684	0.71875	0.90322
Wsr1	1.3446×10^6	1.8216×10^7	5.7689×10^6	9.8787×10^6	4.5293×10^6	9.5534×10^6
Wsc1	0.016903	0.0084157	0.00015914	1.2457×10^{-10}	0.0051843	0.0030387
$\tau_F= R_1\cdot P_1$, c	3.0×10^{-5}	2.2×10^{-4}	1.4×10^{-5}	8.5×10^{-5}	9.3×10^{-5}	9.7×10^{-6}
τ_D, c	3.0×10^{-3}	3.3×10^{-4}	1.4×10^{-4}	9.5×10^{-4}	1.2×10^{-5}	3.6×10^{-6}

The presence of platinum in single crystals is confirmed by X-ray spectral analysis (Fig. 5), and is 3.04 at. % or 8.74 wt.%. for samples doped at 1100°C (Fig. 5a) and 7.38 at. % or 15.48 wt.%. for samples doped at 1200°C (Fig. 5b).



a) b)

Fig. 5. Energy-dispersive spectra of silicon samples doped with platinum at 1100 °C (a) and 1200 °C (b).

The energy-dispersive spectra presented in Figure 5 indicate the presence in the composition of the studied samples, in addition to platinum, oxygen and carbon atoms in a small percentage concentration. Additional experiments were carried out using ellipsometric spectroscopy and the optical parameters of various layers formed on the surface of doped samples were determined. Ellipsometry measures the change in polarization when light is reflected or transmitted from a material structure. The change in polarization is represented as the ratio of the amplitudes Ψ and the phase difference Δ. The measured response depends on the optical properties and thickness of the individual materials. Figure 6 shows the Ψ- and Δ-spectra of the initial, doped and irradiated samples.

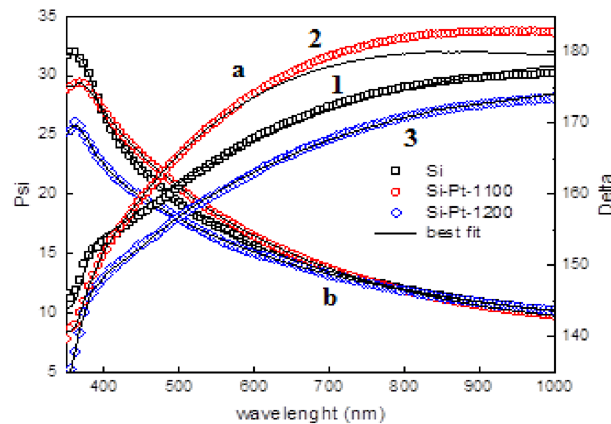


Fig.6. Ψ-spectra (a) and Δ-spectra (b) of samples: 1 - original, 2 - doped with platinum at 1100 °C and 3 - doped with platinum at 1200 °C. the black line is the best fit curve.

It was found that only an oxide layer with a thickness of 5.37 nm was observed in the initial samples (Table 3). After doping with platinum atoms at 1100°C, in addition to the oxide layer, a diffusion layer 21 nm thick appears on the surface of the samples, and the thickness of the oxide layer increased to 10.86 nm. Doping with platinum at a temperature of 1200°C leads to the appearance of a diffusion layer 30.4 nm thick and a decrease in the oxide layer by 8.98 nm (Table 3).

Table. 3. Parameters of oxide and diffusion layers on the surface of silicon samples.

No	Samples	Thickness (nm)	
		Native oxide layer	Diffusion layer
1	Si	5.3772	0
2	Si-Pt-1100°	10.86	21
3	Si-Pt-1200°	8.9791	30.4

It is known that a natural oxide layer is formed on the surface of semiconductor materials in an oxygen atmosphere [22]. Therefore, in the three-layer model used to explain the results of ellipsometric spectroscopy measurements, the natural oxide layer is always taken into account. A three-layer model was used in the calculations, including a natural oxide layer, a diffusion layer, and a crystalline silicon substrate [23]. For the natural oxide layer, the dispersion model of Cauchy and Urbach was used (Fig. 7), and for the diffusion layer of the samples, the parametric Si model was used (Fig. 8).

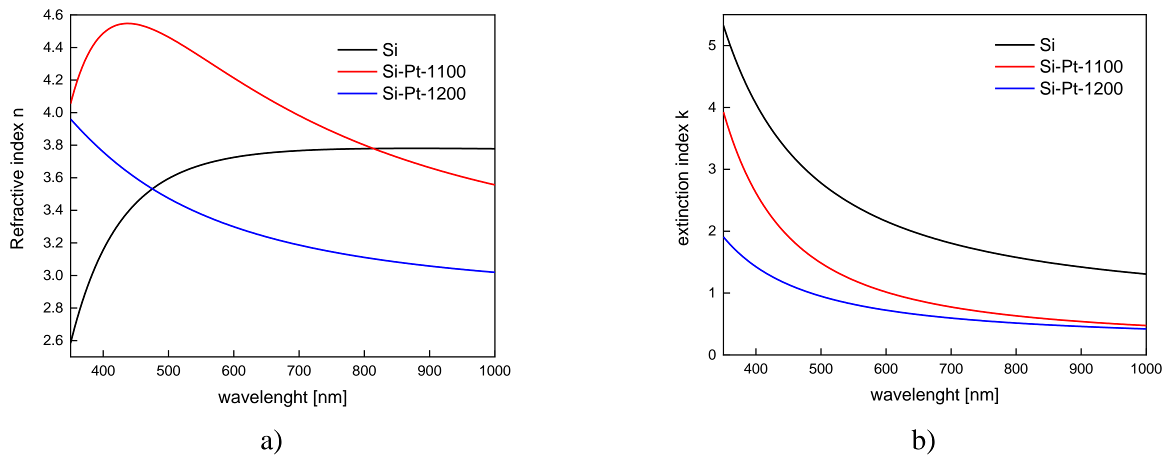
The dispersion models of Cauchy and Urbach give the following dependence of the refractive index n(λ) and the extinction coefficient k(λ) on the light wavelength λ(nm), respectively [24]:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots \quad (3)$$

$$k(\lambda) = \alpha e^{\beta\left(1240\left(\frac{1}{\lambda} - \frac{1}{\gamma}\right)\right)} \quad (4)$$

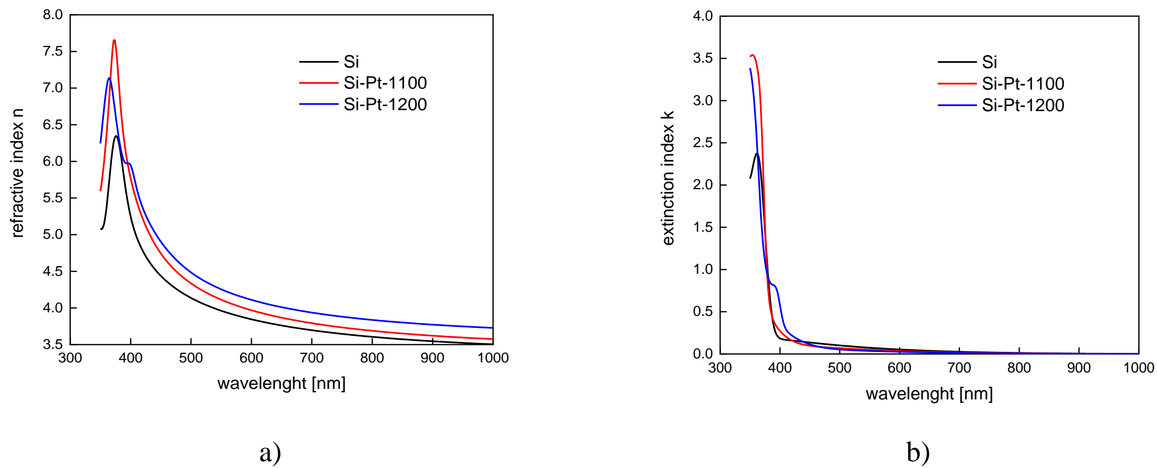
where A, B, C are the Cauchy coefficients, α is the amplitude of the extinction coefficient, β is the exponential factor, and γ is the band edge.

.



a) b)

Fig.7. Optical constant spectra of Cauchy and Urbach: a - refractive index n(λ); b - extinction coefficient k(λ).



a) b)

Fig.8. Optical constant spectra for the diffusion layer of Si samples.
a is the refractive index n(λ); b - extinction coefficient k(λ).

4. Conclusion

Thus, by the method of electrochemical impedance spectroscopy, it was established that doping of n-Si samples with Pt impurity at different temperature conditions contributes to a significant (2-3 times) increase in their electrical conductivity (Table 1). It is shown that the higher the concentration of electroactive platinum atoms, the lower the concentration of radiation defects, and this, in turn, leads to a decrease in the electrical resistance of silicon samples.

It has been found that doping samples at 1200°C increases the radiation resistance of silicon samples. Increasing the doping temperature to 1200°C leads to the appearance of a linear diffusion process in the sample in a homogeneous layer with a slight deviation from Fick's second law.

The mechanism of radiation defect formation is presumably associated with the formation of complexes of radiation defects in the crystal lattice, which change the geometry of the electrical conductivity channels and create reactivity.

Using ellipsometric spectroscopy, the presence of diffusion and oxide layers on the surface of the original and doped samples was established. It has been established that, in the initial samples, implantation leads to the appearance of only an oxide layer 5.37 nm thick. After doping, in addition to the oxide layer, diffusion layers also appear. The thickness of diffusion layers in silicon doped at 1200°C is 1.5 times greater than in silicon samples doped at 1100°C.

Acknowledgment

The authors express their gratitude to the staff of the EG-5 group, the Laboratory of Neutron Physics named after I.M. Frank (JINR) for the practical help of irradiation with protons in this study.

References

1 Utamuradova Sh. B., Rakhmanov D.A. Effect of holmium impurity on the processes of radiation defect formation in n-Si<Pt>. *Physics AUC*, 2022, Vol. 32, pp.132 - 136. https://cis01.central.ucv.ro/pauc/vol/2022_32/15_PAUC_2022_132_136.pdf

2 Sapaev I., Sapaev B., Abdullaev D., Abdullayev J., Umarov A., Siddikov R., Mamasoliev A., Daliev K. Influence of the parameters to transition capacitance at NCDS-PSI heterostructure. *E3S Web of Conferences*, 2023, 383, pp.04022(1-7). doi:10.1051/e3sconf/202338304022

3 Yunusov M.S., Karimov M., Alikulov M.N., Begmatov K.A. The radiation-induced defects production in p-type silicon doped by impurities of transitional elements. *Radiation Effects and Defects in Solids,* 2000, 152(3), pp.171 – 180. doi:10.1080/10420150008211821

4 Utamuradova Sh.B., Stanchik A.V., Rakhmanov D.A. X-ray structural investigations of n-Si<Pt> irradiated with protons. *East Eur. J. Phys*., 2023, 2, pp.201. doi:10.26565/2312-4334-2023-2-21

5 Yunusov M.S., Karimov M., Khalikov P.A. Mechanisms for thermal stability of the electrophysical properties of overcompensated n-Si 〈B,S. *Technical Physics Letters*, 1999, 25(12), pp.969 – 970. doi: 10.1134/1.1262697

6 Yunusov M.S., Akhmadaliev A., Begmatov K.A. Semiconductor detector as ionising radiation dosimeter. *Radiation Physics and Chemistry*, 1995, 46(4-6), Part 2, pp.1287 – 1290. doi: 10.1016/0969-806X(95)00371-4.

7 Utamuradova Sh. B., Stanchik A.V., Rakhmanov D.A., Doroshkevich A.S., Fayzullaev K.M. X-ray structural analysis of n-Si<Cr>, irradiated with alpha particles. *New materials, compounds and applications*, 2022, Vol.6, No. 3, pp. 214 – 219. http://jomardpublishing.com/UploadFiles/Files/journals/NMCA/V6N3/Utamuradova_et_al.pdf

8 Kozlov V.A., Kozlovskiy V.V. Doping of semiconductors with radiation defects upon irradiation with protons and alpha particles. *Semiconductors*, 2001, Vol. 35, Is.7, pp.769-795. https://journals.ioffe.ru/articles/viewPDF/38565 [in Russian]

9 Galeeva A.V. Issledovanie provodimosti poluprovodnikovix struktur metodom impedansnoy spektroskopii. // Avtoreferat. 2010, Moskva. [in Russian]

10 Utamuradova Sh.B., Rakhmanov D.A., Doroshkevich A.S., Kinev V.A., Ponamareva O.Yu., Mirzayev M.N., Isayev R.Sh. IR - spectroscopy of n-Si<Pt> irradiated with protons. *Advanced Physical research*, 2023, Vol.5, No 2, pp.72. http://jomardpublishing.com/UploadFiles/Files/journals/APR/V5N2/Utamuradova_et_al.pdf

11 Turgunov N.A., Berkinov E.H., Mamazhonova D.X. The influence of thermal processing on the electrical properties of silicon, alloyed nickel. *Applied Physics*, 2020, 3, 40. PF-20-3-40.pdf (orion-ir.ru) [in Russian]

12 Shehata M.M., Truong T.N., Basnet R., Nguyen H.T., Macdonald D.H., Black L.E. *Solar Energy Materials and Solar Cells,* 2023, Volume 251, Pp.112167.

13 Vladikova D., Stoynov Z., Raikova G., Thorel A., Chesnaud A., Abreu J., Viviani M., Barbucci A., Presto S., Carpanese P. Impedance spectroscopy studies of dual membrane fuel cell. *Electrochimica Acta*, 56, 2011, pp.7955-7962. doi:10.1016/j.electacta.2011.02.007

14 Nijen D.A., Muttillo A, Dyck R.V., Poortmans J, Zeman M., Isabella O., Manganiello P. Revealing capacitive and inductive effects in modern industrial c-Si photovoltaic cells through impedance spectroscopy. *Solar Energy Materials and Solar Cells,* 2023, 260, 112486. doi:10.1016/j.solmat.2023.112486

15 Srivastava A., Sharma D., Srivastava S.K. Impedance spectroscopy analysis to probe the role of interface properties of surface micro-engineered PEDOT:PSS/n-Si solar cells. *Organic Electronics*, 2023, Volume 119, 106817. doi:10.1016/j.orgel.2023.106817

16 Utamuradova Sh.B., Rakhmanov D.A., Doroshkevich A.S., Genov I.G., Slavkova Z., Ilyina M.N. Impedance spectroscopy of p-Si<Pt>, p-Si<Cr> irradiated with protons. *Advanced Physical research*, 2023, Vol.5, No 1, pp.5-11. http://jomardpublishing.com/UploadFiles/Files/journals/APR/V5N1/Utamuradova_et_al.pdf

17 Turgunov N.A., Berkinov E.Kh., Mamajonova D.X. Decay of impurity clusters of nickel and cobalt atoms in silicon under the influence of pressure. *Journal of Nano- and Electronic Physics*, 2021, 13(5), 05006. doi:10.21272/jnep.13(5).05006

18 Raikova G., Vladikova D., Stoynov Z. Differential impedance analysis of the cathode compartment in dual membrane fuel cell. *Bulgarian Chemical Communications*, 2011, Vol.43, Is.1, pp.133 – 137.

19 Stoynov Z.B., Vladikova D.E., Abrashev B.I., Slavova M.P., Burdin B.G., Mihaylova-Dimitrova E.S., Colmenares L.C., Mainar A.R., Blázquez J.A. Screening impedance analysis of Zn-air cells. *Bulgarian Chemical Communications*, 2018, Vol.50. pp.189 – 194.

20 Daliev K.S., Ahmedov M.M., Onarkulov M.K. Influence of the Temperature and Cyclic Deformations of $(Bi_xSb_{1-x})_2Te_3$ Films on Their Resistance. *Journal of Engineering Physics and Thermophysics*, 2021, 94(5). pp.1369–1373. doi: 10.1007/s10891-021-02419-1

21 Turgunov N.A., Berkinov E.Kh., Turmanova R.M. Accumalations of impurity Ni atoms and their effect on the electrophysical properties of Si. *E3S Web of Conferences,* 2023, Vol. 402, pp.14018(1-8). doi:10.1051/e3sconf/202340214018

22 Utamuradova Sh.B., Daliev Sh.Kh., Stanchik A.V., Rakhmanov D.A. Raman spectroscopy of silicon, doped with platinum and irradiated by protons. *E3S Web of conferences,* 2023, Vol. 402. pp.14014(1-9) Vol.10.1051/e3sconf/202340214014

23 Turgunov N.A., Berkinov E.Kh., Turmanova R.M. The effect of thermal annealing on the electrophysical properties of samples n-Si<Ni,Cu>. *East European Journal of Physics*, 2023, 3, pp.287-290. doi:10.26565/2312-4334-2023-3-26

24 Tuan P.L., Kulik M., Nowicka-Scheibe J., Żuk J., Horodek P., Khiem L.H., Phuc T.V., Anh, Nguyen Ngoc., Turek M. Investigations of chemical and atomic composition of native oxide layers covering SI GaAs implanted with Xe ions. *Surface and Coatings Technology,* 2020, Vol 394. doi: 10.1016/j.surfcoat.2020.125871

Article accepted for publication 17.06.2023