Physics of the Solid State, 2025, Vol. 67, No. 12

03,09,14

Influence of neutron-doped phosphorus isotope on the microhardness of monocrystalline silicon

© *Sh. Makhkamov*[1], *M.Yu. Tashmetov*[1], *M.N. Erdonov*[1], *N.B. Ismatov*[1], *Sh.A. Makhmudov*[1], *Sh.M. Nazarmamatov*[1], *Kh.M. Kholmedov*[2]

[1] Institute of Nuclear Physics, Uzbek Academy of Sciences,
Tashkent, Uzbekistan
[2] Tashkent Al-Khwarizmi University of Information Technologies,
Tashkent, Uzbekistan
E-mail: rdonov@inp.uzmuzaffarerdonov1978@yandex.ru, makhkamov@inp.uz

Received November 15, 2025
Revised December 1, 2025
Accepted December 2, 2025

The change in microhardness of initial n- and p-type silicon containing phosphorus and boron impurities during neutron transmutation was investigated. It was found that doping silicon with the stable isotope ^{31}P, regardless of the phosphorus content in the original crystal, leads to an increase in the microhardness of n-Si$\langle\mathrm{P}\rangle$. For p-type silicon containing boron impurities, microhardness is determined by the ratio of boron and ^{31}P isotope concentrations. It was established that in p-Si$\langle\mathrm{B}\rangle$, an increase in microhardness of neutron-transmutation p-type silicon is observed when the concentration ratio $\mathrm{N}_{^{31}\mathrm{P}}/\mathrm{N}_\mathrm{B} > 1$. The mechanism of transformation of radiation-induced and intrinsic defects responsible for the change in microhardness of n- and p-type silicon during neutron transmutation is discussed.

Keywords: monocrystalline silicon, impurity, neutron-transmutation silicon, doping, isotope ^{31}P, concentration, microhardness.

DOI: 10.61011/PSS.2025.12.63078.325-25

1. Introduction

The microhardness of crystals characterizes the quality and strength of semiconductor materials and is one of the important physical and mechanical properties. Among semiconductor crystals, neutron transmutation silicon is one of the basic materials for the production of power semiconductor devices, where the main requirements are a high uniformity of the distribution of alloying impurities throughout the crystal volume and a minimum radial change in resistivity across the plate. The dependence of the degree of transmutation doping of a crystal on the irradiation time at a constant neutron flux density makes it possible to regulate the concentration of the introduced isotopic impurity ^{31}P over a wide range with high accuracy and obtain monocrystalline silicon with specified electrophysical parameters. The features of nuclear doping of elementary semiconductors and semiconductor compounds are given in Ref. [1], where the influence of various factors on the properties of nuclear transmutation crystals is considered.

Based on measurements of the microdistribution of resistivity (ρ) in nuclear-doped silicon with a plate diameter of $\simeq 40$ mm it was shown in Ref. [2] that the distribution of the isotope ^{31}P in the sample volume is characterized by high uniformity. The authors of Refs. [3,4] proposed methods for obtaining neutron transmutation silicon with radial uniformity in resistivity for ingots with a diameter of 200 mm with a deviation of ρ to 2 % across the plate. However, it was found in Refs. [2,5] that the presence of oxygen impurities and phosphorus atoms in neutron transmutation silicon during annealing leads to a redistribution of ^{31}P in the crystal volume. The effect of heat treatment on the electrical and thermoelectric characteristics of silicon crystals doped by nuclear transmutation is considered in Ref. [6]. It is shown that the optimal value of the thermoelectric quality factor of nuclear-doped silicon is achieved by choosing the temperature and duration of annealing, as well as the cooling rate after thermal annealing.

The authors of Ref. [7] proposed a facility for neutron transmutation doping (NTD) of silicon with a diameter of 203 mm and a length of up to 500 mm, which reduces the uneven irradiation of ingots to 5 % by using a graphite reflector and a thermal neutron filter. The improvement of the radial uniformity of NTD silicon carbide to 1 % was achieved in Ref. [8] by rotating the ingot during irradiation and optimizing the size of the neutron exit slit. The authors of Ref. [9] irradiated the samples in the IVV-2M research reactor at a neutron flux density of $1.46 \cdot 10^{12}\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$ for 168 h to obtain a stable, uniformly distributed impurity of the ^{31}P isotope with a concentration of $10^{14}\,\mathrm{cm}^{-3}$ in thin silicon films with a thickness of 5 and 15 μm. It was shown in Ref. [10] that adjusting the reactor spectrum using neutron absorbers makes it possible to adjust the value of ρ and the silicon doping concentration of ^{31}P over a wide range in one irradiation cycle. The possibility of using the doped isotope ^{31}P in case of NTD to determine the absolute values of the reactor thermal neutron density in the fluence range $10^{12}-10^{18}\,\text{cm}^{-2}$ is shown in Ref. [11]. The authors of Ref. [12] present results on reducing the spread of electrical resistivity over the volume of a silicon ingot (especially in height) by using a cadmium shield exposure device for silicon NTD in a nuclear reactor.

The authors of Ref. [13] found a nonmonotonic change in the microhardness of monocrystalline silicon at low doses of electron irradiation.

An analysis of the literature data shows that the main research results are devoted to the study of the effect of irradiation and annealing modes on the electrophysical parameters of nuclear transmutation silicon, while information on the physico-mechanical properties of NTD silicon, depending on the initial type of conductivity and phosphorus or boron content, is practically not identified in the literature. Given that silicon is one of the most important structural materials in microelectronics and its widespread use in the manufacture of various hybrid semiconductor devices and other products, in addition to electrophysical parameters, there are also requirements for physical and mechanical properties, in particular microhardness. The latter is determined by the degree of uniformity of doping, the state of the formed structural and intrinsic defects, the type and content of impurities in the crystal, as well as their interaction during neutron transmutation and annealing of irradiated samples.

Previously, we studied the effect of electron irradiation on the microhardness of silicon doped with an admixture of cobalt in the work of Ref. [14]. At the same time, a decrease in the microhardness of silicon was found with an increase in the degree of doping of *n*-type silicon with cobalt. It is shown that electron irradiation of samples from Si⟨Co⟩ with an energy of 4 MeV leads to an increase in the microhardness of both the initial and doped silicon. However, the efficiency of increasing microhardness in unalloyed samples remains higher compared to cobalt-doped silicon. Similar results were obtained when silicon was doped with germanium [15], where the microhardness of monocrystalline silicon decreased with increasing concentration of germanium.

The purpose of this paper is to study changes in the microhardness of silicon single crystals with different contents of the initial phosphorus or boron admixture doped with the isotope ^{31}P as a result of neutron transmutation.

2. Experimental methodology

Silicon grown by the Chokhralsky method with a concentration of initial phosphorus ranging from $4\cdot10^{13}$ to $4.3\cdot10^{14}\,\text{cm}^{-3}$, boron from $1.2\cdot10^{14}$ to $2.5\cdot10^{15}\,\text{cm}^{-3}$ and oxygen $\sim 7\cdot10^{17}\,\text{cm}^{-3}$ and dislocation density $\sim 10^{4}\,\text{cm}^{-2}$ was used for *n*-Si⟨P⟩ and *p*-Si⟨B⟩ nuclear transmutation doping. Neutron irradiation of silicon wafers with a diameter of ≈ 45 mm was carried out at a temperature no higher than 60 °C in the channel of the VVR-SM reactor in the fluence range from 10^{16} to $4\cdot10^{18}\,\text{n/cm}^2$ followed by isochronous annealing of NTD silicon at a temperature of 800 °C. $2\times4\times8$ mm samples containing different initial concentrations of phosphorus or boron were made from these *n*- and *p*-Si plates. The change in the concentration of the main current carriers of the samples was determined by the Hall coefficient at room temperature, while the deviation of the radial uniformity values of the neutron-doped (ND) plates did not exceed 1 %. In parallel with ND silicon, unirradiated samples of *n*- and *p*-Si were also annealed. The measurement of microhardness (H) was carried out using a digital microhardness tester HVS-1000 by the Vickers method on the plane ⟨111⟩ at an indenter load of 50 g and a loading time of 20 seconds. The resolution of the micrometer when measuring the diagonal of the indentor imprint was $0.01\,\mu$m, microhardness values (HV) were measured using the Vickers method and averaged based on the results of 5 measurements. Then, using the well-known formula

$$HV = 1.854\cdot F/d^2$$

the microhardness value was calculated, where F is the applied load, d is the arithmetic mean of the diagonals of the rhombic prints.

3. Experimental results and their analysis

The concentrations of current carriers in *n*- and *p*-type silicon were measured before and after annealing at 800 °C for 2 h to control the electrophysical parameters of neutron-doped samples. It was revealed that the concentration of current carriers in both *n*- and *p*-Si decreases with increasing integral dose of neutron irradiation. This is due to the formation of disordered regions and the formation of a number of spectra that compensate for the deep energy levels of radiation defect centers and their complexes: the acceptor type in *n*-Si and the donor type in *p*-Si. These centers, located in the upper and lower half of the silicon band gap at a distance of 0.16 to 0.45 eV from the bottom of the conduction band and the ceiling of the valence band and being traps of current carriers, lead to a significant increase in the value of ρ. An analysis of the position of deep RD centers formed in the initial and neutron-transmutation Si doped with the ^{31}P isotope when irradiated with ^{60}Co gamma quanta, fast electrons and neutrons shows that the energy levels of the main RD centers have almost similar values, which confirms the Hall measurements NTD samples before and after annealing. We have shown in Ref. [16] that both without heating and with combined temperature exposure and electron irradiation with energy 4 MeV or by ^{60}Co gamma quanta, known deep levels with the following energy values are formed in silicon of *n*-type: E_c — 0.17 eV (V + O), divacancy (VV) E_c — 0.23 eV and E_c — 0.39 eV, E_c — 0.44 eV (V + P), which exhibit thermal stability from 160 °C to 320 °C. Additional levels with $E_c - 0.13$ eV and $E_c - 0.20$ V are formed at irradiation temperatures of ≥ 350 °C, which the authors of Ref. [17] associate with the formation of oxygen vacancy

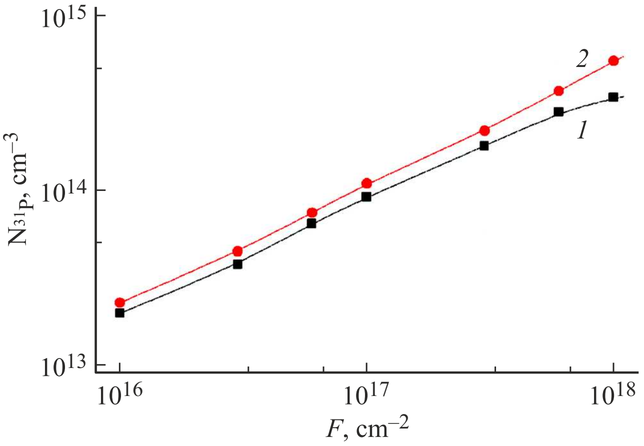

Figure 1. Dependence of the concentration of ^{31}P in n- and p-type silicon on the fluence of neutron irradiation after annealing at 800 °C: *1* — experiment, *2* — calculation.

complexes V_2O_2 and V_3O_2 with thermal stability up to 530 °C. An additional level of $E_V - 0.45\,\mathrm{eV}$ (V+B) is formed in silicon of p-type which is thermostable up to 220 °C. However, as experimental data show, during heat treatment of neutron-irradiated Si samples at 800 °C for ≈ 2 h, complete annealing of point defects and all formed compensating radiation defects and their complexes occurs [1], and the concentration of majority charge carriers in silicon n- increases as a result of the formation of a shallow stable donor level of the ^{31}P impurity with $E_c - 0.045\,\mathrm{eV}$, i.e., annealing is an integral part of the technological process for normalizing the parameters of neutron-transmutation-doped silicon. For p-Si, the change in the concentration of current carriers is determined by the boron content in unirradiated silicon and the concentration of the isotope ^{31}P formed during neutron transmutation. The formed shallow donor level in the upper half of the band gap leads to additional compensation p-Si$\langle$B$\rangle$. As a result, the type of conductivity and concentration of current carriers after annealing of neutron-doped p-silicon depend on the ratio of concentrations of the initial boron and isotope ^{31}P. It should be noted that during neutron irradiation of silicon, one of the three naturally stable isotopes — ^{30}Si, when interacting with thermal neutrons by the reaction ^{30}Si $(n,\gamma)^{31}\mathrm{Si} \xrightarrow{\beta-1} {}^{31}\mathrm{P}$, turns into a donor stable isotope ^{31}P, and the excited nuclei of ^{31}Si go into a stationary state, emitting βparticles and gamma quanta, whose energies are sufficient to form radiation defects, i.e., when exposed to thermal neutrons on Si, regardless of the initial type of crystal conductivity, they are formed as an isotope ^{31}P and the above thermally unstable radiation defect centers.

Change in the concentration of ^{31}P in silicon of n- and p-type depending on the fluence of neutron irradiation to $2 \cdot 10^{18}\,\mathrm{cm}^{-2}$ after annealing at 800 °C for 2 h is shown in Figure 1 (curve *1*). As can be seen, the concentration of the formed isotope ^{31}P increases with increasing dose of neutron irradiation and does not depend on the initial type of silicon. To compare the experimental data obtained, taking into account the irradiation modes and the proportion of slow neutrons in the total reactor neutron flux, the concentration of the introduced ^{31}P was calculated (Figure 1, curve *2*) using the formula:

$$\mathrm{N}(^{31}\mathrm{P}) = \mathrm{N} \cdot \mathrm{K}\sigma\varphi t,$$

where N is the number of silicon atoms in $1\,\mathrm{cm}^{-3}$, K is the relative content of the isotope ^{30}Si in a natural mixture, σ is the effective cross-section of radiation capture of thermal neutrons in ^{30}Si, φ is slow neutron flux density, t is irradiation time.

Measurements of the Hall coefficient and calculation of the concentration of ^{31}P in silicon samples annealed at 800 °C after neutron irradiation in the fluence range from 10^{16} to $2 \cdot 10^{18}\,\mathrm{cm}^{-2}$ showed that the experimental and calculated values of N(^{31}P) are in good agreement.

Microhardness dependences (H) of silicon n- and p-type containing different concentrations of phosphorus (N_P) or boron (N_B) in nonradiated crystals, after neutron irradiation and subsequent annealing are shown in Figures 2 and 3. The results showed that in n-Si, with an increase in the concentration of the isotope ^{31}P, the microhardness of the ND samples increases, while the efficiency of changing the value H is affected by the phosphorus content in the unirradiated samples (Figure 2). An increase in the phosphorus concentration in an unirradiated crystal from $4 \cdot 10^{13}$ to $4.3 \cdot 10^{14}\,\mathrm{cm}^{-3}$ after annealing of neutron-doped samples leads to an increase in H from 7% to 12%, respectively (Figure 2, curves *2, 4*).

It should be noted that a slight increase in microhardness in neutron-doped n-Si$\langle$P$\rangle$ samples was also detected before annealing, which may be due to the transformation of interstitial intrinsic defects ^{30}Si, leading to an increase

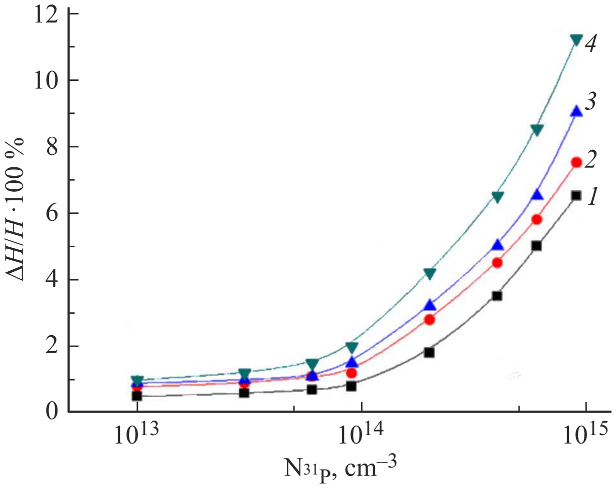

Figure 2. Relative change in the microhardness of neutron-doped silicon of n-type depending on the isotope concentration ^{31}P: after irradiation (*1, 3*) and after heat treatment at 800 °C (*2, 4*). Phosphorus content in the initial n-Si; cm^3: *1, 2* — $4 \cdot 10^{13}$; *3, 4* — $4.3 \cdot 10^{14}$.

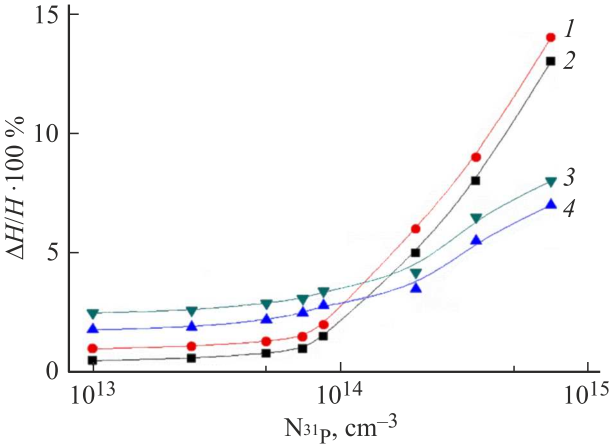

Figure 3. Relative change in microhardness in neutron-doped silicon *p*-type depending on the isotope concentration ^{31}P: after irradiation (*2, 4*) and after heat treatment at 800 °C — (*1, 3*); boron content in the initial *p*-Si; cm^{-3}: *1, 2* — $1.2\cdot10^{14}$; *3, 4* — $2.5\cdot10^{15}$.

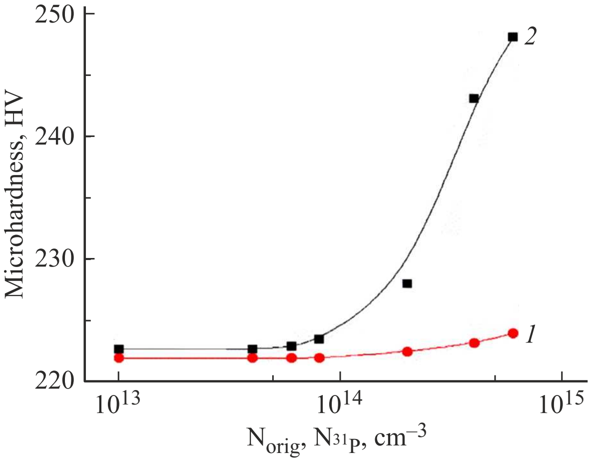

Figure 4. Dependence of the microhardness of *n*-Si on the concentration of phosphorus and isotope ^{31}P after annealing 800°C: *1* — without isotope ^{31}P; *2* — isotope-doped ^{31}P.

in the energy of interatomic bonds of the silicon crystal lattice. The contribution of the initial concentration P(N_{initial}) and the isotope content ^{31}P($N_{^{31}\mathrm{P}}$), taking into account their total concentration ($N_{\mathrm{initial}} + N_{^{31}\mathrm{P}}$), to the change in the microhardness of neutron-doped silicon is shown in Figure 4. As can be seen from a comparison of the microhardness of irradiated and unirradiated *n*-Si samples with an identical total phosphorus concentration under the condition ($N_{\mathrm{P}} = N_{\mathrm{initial}} + N_{^{31}\mathrm{P}}$), an increase of N_{P} in unirradiated silicon within the concentration range of 10^{13} cm^{-3} to $7\cdot10^{14}$ cm^{-3} has practically no effect on the microhardness value (Figure 4, curve *1*). However, an increase in the total phosphorus concentration (Ninitial + $N_{^{31}\mathrm{P}}$) in silicon ND to values characteristic of unirradiated samples leads to an increase in microhardness to 14 %, for *n*-Si with $N_{\mathrm{initial}} \simeq 8\cdot10^{14}$ cm^{-3}.

The change in the microhardness of the neutron-doped *p*-Si⟨B⟩ (Figure 3) differs from the behavior of *n*-Si⟨P⟩. The study of the microhardness of the initial boron-doped silicon (Si⟨B⟩), a slight change in microhardness *H* was found depending on the boron concentration in the range of $1.2\cdot10^{14}$–$2.5\cdot10^{15}$ cm^{-3} . Neutron irradiation of these samples showed that the change in microhardness (Figure 3, curve *1–4* in *p*-Si⟨B⟩ depends on the boron content (N_{B}) in unirradiated silicon and is determined by the concentration ratio N_{B} and $N_{^{31}\mathrm{P}}$ of the ^{31}P isotope produced in case of neutron transmutation. It was found that a slight decrease in microhardness is observed at the ratio of $N_{^{31}\mathrm{P}}/N_{\mathrm{B}} < 1$ compared with the unirradiated *p*-Si⟨B⟩, with a plateau at $N_{\mathrm{B}} \approx N_{^{31}\mathrm{P}}$. With a further increase in the ratio of $N_{^{31}\mathrm{P}}/N_{\mathrm{B}} > 1$, with an increase in the concentration of ^{31}P, the microhardness begins to increase and is determined by the dose of neutron irradiation of silicon. Annealing of irradiated samples at 800 °C for 2 h leads to an additional increase in the microhardness of *p*-Si⟨B⟩ to 12 % with a concentration of $N_{\mathrm{B}} = 1.2\cdot10^{14}$ cm^{-3} (Figure 3 curve *1*). This behavior of microhardness in *p*-Si⟨B⟩ and *n*-Si⟨P⟩ may be associated with a decrease in the concentration of point and radiation defect complexes due to their annihilation on dislocations during annealing, as well as with a decrease in the magnitude of internal elastic stresses with an increase in the concentration of ^{31}P in *n*-Si⟨P⟩. In the case of *p*-Si⟨B⟩, the increase in microhardness may be associated with a decrease in the silicon lattice parameter due to a decrease in the covalent bond length in Si⟨B⟩ when the phosphorus isotope is introduced.

It should be noted that isochronous annealing of non-irradiated initial silicon of *n*- and *p*-type at 800 °C for 2 h did not lead to a noticeable change in the microhardness of the samples.

Thus, it was found that the efficiency of changing the microhardness of neutron-doped *n*-Si⟨P⟩ and *p*-Si⟨B⟩ is determined by the phosphorus or boron content in the initial silicon and the concentration of transmutation ^{31}P. An increase in the content of N_{P} and $N_{^{31}\mathrm{P}}$ in *n*-Si leads to an increase in microhardness, while an increase in the content of N_{B} in *p*-Si, in the region of low concentrations of ^{31}P i. e. $N_{^{31}\mathrm{P}} < N_{\mathrm{B}}$ contributes to its reduction during neutron doping.

4. Conclusion

As a result of studies of the microhardness of neutron transmutation silicon containing phosphorus or boron impurities, it was found that the effectiveness of increasing microhardness at identical concentrations of N_{P}, N_{B} and neutron doping modes in *n*-Si⟨P⟩ higher than in *n*-Si⟨B⟩, and is determined by the concentration of the radionuclide ^{31}P. It was found that in neutron-doped silicon of the *p*-type containing boron impurities, an increase in microhardness is observed at a concentration ratio of $N_{^{31}\mathrm{P}}/N_{\mathrm{B}} > 1$.

Funding

This study is financed from state budge funds of the Republic of Uzbekistan.

Conflict of interest

The authors declare no conflict of interest.

References

[1] Voprosy radiatsionnoy technologii poluprovodnikov / Pod red. L.S. Smirnova, Novosibirsk: „Nauka“. (1980). p. 296 (in Russian).

[2] W.E. Has, M.C. Schnoller. Silicon Doping by Nuclear Transmutation // Electronic materials. **5**, *1*, 57 (1978).

[3] Artur Wilson Carbonari. Proceedings of the 4 Brailian meeting on Nuclear Applications, **2**, 71 (1997).

[4] L. Anders, M. Græsvænge, C. Hindrichsen. J. Cryst. **512**, 65 (2019). DOI: 10.1016/j.jcrysgro.2019.02.017

[5] I.M. Greskov, S.P. Solovyov, V.A. Kharchenko. FTP **11**, *8*, 1598 (1977) (in Russian).

[6] G.P. Gaidar. Elektronnaya obrabotka materialov, **56**, *6*, 61 (2020) (in Russian).

[7] I.I. Lebedev, D.E. Zolotykh, A.G. Naymushin, N.V. Smolnikov, M.N. Anikin, V.A. Varlachev. Atom Indonesia **47**, *1*, 39–44 (2021). DOI: ttps://doi.org/10.17146/aij.2021.1005

[8] Do Hyun Kim, Han Rim Lee, Jiseok Kim, Myong-Seop Kim, Byung Gun Park. Journal of the Korean Physical Society **79**, 12–18 (2021). https://doi.org/10.1007/s40042-021-00178-z

[9] Andrey Isakov, Sergey Khvostov, Evgeny Kinev, Michael Laptev, Anastasia Khudorozhkova, Olga Grishenkova, Vladimir Rychkov and Yurii Zaikov. Journal of The Electrochemical Society **167**, *8*, (2020). https://doi.org/10.1149/1945-7111/ab933c.

[10] J. Van de Pitte, J. Wagemans, A. Gusarov, I. Uytdenhouwen, C. Detavernier, J. Lauwaert. NUCLEAR TECHNOLOGY 2020. American Nuclear Society https://doi.org/10.1080/00295450.2019.1697172

[11] V.A. Varlacheva, E.G. Emetsa, Yu. Mua, E.A. Bondarenkoa, V.A. Govorukhina. Instruments and Experimental Techniques **65**, *6*, 887–890 (2022).

[12] A.A. Shaimerdenov, N.K. Romanova, D.S. Sayranbaev, S.H. Gizatulin. Vestnik NYAC RK **3**, 9–14 (2021) (in Russian).

[13] Yu.I. Golovin, A.A. Dmitrievsky, I.A. Pushnin, N.Yu. Suchkova. FTT **46**, *10*, 1790 (2004) (in Russian).

[14] M.Yu. Tashmetov, Sh. Makhkamov, M.N. Erdonov, R.P. Saidov, N.T. Sulaymanov, T.S. Tillaev, Kh.M. Kholmedov. AIP Conf. Proc. **3020**, 040006 (2024).

[15] S.A. Vabishevich, N.V. Vabishevich. D.I. Brinkevich. Vestnik polockogo gosudarstvennogo Universiteta. Seriya S. Fundamental'nye nauki **3**, 109 (2010) (in Russian).

[16] Sh. Makhkamov, M.Yu. Tashmetov, M.N. Erdonov, R.P. Saidov, H.M. Kholmedo. XIII International Scientific school-conference on radiation physics, dedicated to the 90th anniversary of A.A. Alybakov — founder of solid state physics in the Kyrgyz Republic. July 31–August 6. p. 15–18 (2023) (in Russian).

[17] E.A. Tolkacheva, V.P. Markevich, L.I. Murin. FTP **52**, *9*, 973 (2018) (in Russian).

Translated by A.Akhtyamov