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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEFECT FORMATION PROCESSES IN THE NUCLEUS OF NANO-SILICON AS A RESULT OF EPITHERMAL NEUTRON SCATTERING AND RADIATION CAPTURE

Specialty: 2222.01- Physics and technology of nanostructures;
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Field of science: Physics

Applicant: **Aydan Adil Garibli**

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The dissertation was performed at the department of "Chemical Physics of Nanomaterials" of Baku State University

Scientific supervisors: Professor **Mahammadali Ahmad Ramazanov**

Professor **Borut Smodis**

Official opponents: Corresponding member of ANAS, Dr. in Physics and Mathematics, Professor **Salima Ibrahim Mehdiyeva**

Academician, Dr. in Physics and Mathematics, Professor **Oktay Kazim Gasymov**

Dr. in Physics, Associate Professor **Nushaba Nubarak Hajiyeva**

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Chairman of the Dissertation council: Dr. in Physics, Academician

______________ **Anvar Pirverdi Nahmadov**

Scientific secretary of the Dissertation council: Ph.D. in Physics

______________ **Aynura Alisa Hadiyeva**

Chairman of the scientific seminar: Dr. in Physics, Academician

______________ **Ogtay Abil Samadov**

GENERAL DESCRIPTION OF THE WORK

Relevance of the topic. Silicon is one of the main materials of modern solid state electronics. According to experts, in the next 30-40 years silicon and materials based on it will retain their leadership in microelectronics, power electronics, solar electronics, micromechanics, nuclear and space technologies. However, silicon-based equipment and materials do not meet all the requirements of the rapidly developing scientific and technical fields mentioned above. Therefore, in recent years extensive research has been carried out in the direction of reducing the size of silicon crystals to nanoscale, determining their composition, physical properties, and new methods of modification. From this point of view, the study of the effect of various radiation, and in most cases of the neutron flux, on the modification of nanoscale silicon, its composition and properties is one of the most promising scientific directions.

Silicon is now also widely used as a solar energy converter. To modify its electrophysical properties, phosphorus nuclei are introduced by a nuclear reaction ${}^{30}_{14}Si\,(n\,,\beta\,){}^{31}_{15}\,P$. In this case, both charge carriers and the conversion efficiency of solar energy change in silicon. Consequently, under neutron irradiation, additional non-equilibrium charge carriers can be formed in the base materials under the action of radiation emitted by radioactive isotopes as a result of transformations of the base and mixed atomic nuclei of microelectronic materials. As a result of these processes, strong changes in the electrical and dielectric properties of materials occurs.

Therefore, the topic of the presented dissertation work is devoted to the study of the characteristic parameters of the processes of interaction of epithermal neutrons with high energy and flux density with the scattering mechanisms, the regularities of the processes of radioactive decay and scattering in mixed and basic nano-silicon nuclei, a determination of the energy transferred to the medium and defect formation processes under the influence of these processes, as well as the resulting changes in electrophysical and dielectric properties, is relevant and is of great fundamental, scientific and practical importance.

Purpose of the dissertation: The main purpose of the dissertation is the theoretical and experimental study of the interaction of the nuclei of natural silicon isotopes and non-controlled mixed elements that make up nano-silicon with neutrons with different energies by the mechanism of elastic scattering and radiative capture, revealing the regularities of the effect of defects arising on the electrical and dielectric properties of nano-silicon as a result of the transfer of energy into the environment due to these processes.

Research objects.

Nano-silicon synthesized by Sky Spring Nanomaterials Inc., Houston, USA was taken as the object of research. The size of silicon particles was of the order of d ~$100\ nm$, the specific surface area was $S = 80\ m^2/g$, the density was $0.08\ g/cm^3$, and the density of the silicon element in its composition was $C_{Si} = 99\%$.

To achieve this goal, the following studies were planned:

1. Determination of the parameters of the processes of interaction with the nuclei of natural isotopes of silicon present in the composition of nano-silicon at the values of the energies and fluxes of neutrons of the nuclear reactor where the research was carried out.

2. Evaluation of defects and energy transferred to the environment by radiation emitted by radioactive isotopes formed as a result of elastic scattering and radiative capture of neutrons present in the study conditions with natural silicon isotopes and nuclei of mixed elements contained in nano-silicon.

3. Determination of the kinetics of decay processes of radioactive isotopes formed by the interaction of neutrons and nuclei containing nano-silicon by the mechanism of radiation capture, the type of emitted radiation, their energies, and, ultimately, the concentration of elements in nano-silicon.

4. Investigation of changes in fragments of the structure of nano-silicon in the surface-adsorbed phase under the influence of neutrons by Fourier IR-spectroscopy.

5. X-ray structural study of changes in the structural ordering of nano-silicon under the effect of neutrons.

6. Identification of paramagnetic defects formed in nano-silicon under the effect of neutrons and study of changes in their density by the method of Electron Paramagnetic Resonance.

7. Effect of processes occurring under the effect of neutrons on the electrical conductivity and impedance of nano-silicon.

8. Study of the effect of processes proceeding under the effect of neutrons on the dielectric properties of nano-silicon at different values of temperature, field frequency and neutron flux.

9. On the basis of the results obtained, present the mechanisms of the processes occurring in nano-silicon under the effect of a neutron flux and changes in their physical properties under their effect.

The main provisions for the defense:

1. Determination of the characteristic parameters of the interaction of a high-energy neutron flux with natural isotopes that make up nano-silicon.

2. The energy transferred to nano-silicon by irradiation and the processes of defect formation on the example of the radioactive isotope Si-31, formed as a result of radiation capture.

3. Establishment of the decay processes of radioactive isotopes formed as a result of radiation capture processes under the effect of neutrons, the type and energy of the emitted radiation and, ultimately, the determination of the density of nuclei of mixed elements.

4. Results of investigation of defects and structural inhomogeneities caused by nuclear and radiation processes in nano-silicon under the influence of neutrons by methods of X-ray diffraction, Fourier IR-spectroscopy, EPR and SEM.

5. Effect of defects caused by nuclear and radiation processes in nano-silicon under the influence of neutrons on the electrical conductivity of nano-silicon depending on the radiation dose, frequency of the electric field and temperature.

6. Results of studying the effect of nuclear and radiation processes occurring in nano-silicon under the effect of neutrons on the dielectric properties of nano-silicon depending on temperature, field frequency and radiation dose.

7. Generalization of nuclear and radiation processes occurring when a neutron flux in the $625 \div 1 \cdot 10^5$eV energy range on nano-silicon, energy transfer to the medium, defect formation, electrical conductivity and dielectric properties of defective samples.

Scientific novelty.

In the thesis:

1. The parameters of the processes of interaction of silicon isotopes with nuclei during irradiation of nano-silicon with neutrons with $625 \div 1 \cdot 10^5$eV energy with total fluence $\Phi = 1.92 \cdot 10^{13} \text{neutron/cm}^2$, the concentration of new isotopes, including the radioactive isotope Si-31, which can be formed as a result of interaction by the mechanism of radiation capture, the energy given to the medium as a result of their gamma and beta decays and the density of nonequilibrium charge carriers that can arise as a result of ionization have been determined.

2. A method for modifying the electrophysical properties of nano-silicon by introducing the P-31 isotope by the method of radiation doping by irradiating it with neutrons has been revealed.

3. The kinetics of decay of radioactive isotopes formed in nano-silicon as a result of interaction of neutrons by the mechanism of radiation capture, the energy of the emitted rays and the concentration of interacting nuclei have been determined.

4. Structural fragments arising in nano-silicon under the action of neutrons and ordering, regularities of changes at the surface levels have been revealed.

5. ESR-identification of biographical and paramagnetic radiation defects caused by neutron irradiation of nano-silicon have been carried out.

6. The effect of nano-silicon defects on electrical conductivity as a result of processes occurring under neutron irradiation has been studied. The dependences of the real and imaginary parts of the electrical conductivity on temperature, field frequency and neutron flux are found. The regularities of the influence of the field frequency and neutron flux on the activation energy of electrical conductivity are revealed. It was found that charge carriers in nano-silicon are mainly localized at three types of levels. With an increase

in the neutron flux and the frequency of the electric field, the activation energies decrease.

7. The dependence of the real and imaginary parts of the dielectric constant of nano-silicon under irradiation with neutrons on the frequency, temperature and neutron flux has been found.

The practical value of the work. The results obtained on elastic scattering, radiation capture, radioactive decay processes and the combined effect of ionizing radiation emitted into the medium under the influence of neutrons, the main driving force of nuclear transformations, on nanoscale silicon containing three natural isotopes, is of great importance for nuclear physics, radiation materials science and nanoscale physics. In nuclear reactors of a new generation, which will be commissioned in the future, it is planned to create fuel cells based on silicon-uranium. The revealed patterns of processes occurring in silicon-containing materials under the action of neutrons can be used to ensure the safety of the core of these reactors from the point of view of neutron balance and material stability.

On the other hand, the change under the effect of neutron radiation in the properties of nanosized silicon samples, widely used in microelectronics, solar converters, for the detection of high-energy particles can be used in radiation materials science to identify ways to control the properties and increase the efficiency and sensitivity of devices and other systems based on them.

Approbation of research results. The obtained dissertation materials, covering the effect of neutrons on nano-silicon and the processes occurring during this, were presented at various republican and international conferences, symposia and seminars.

1. Neutron activation analysis of silicon nanoparticles. 10th international conference, Nuclear and Radiation Physics, Kurchatov c.,Kazakhstan, 8–11September, 2015, p. 32-33
2. Electrical Conductivity- Temperature Dependencies of nano silicon particles exposed to neutron irradiation, Modern trends in physics, İnternational conference, Baku State University, Baku, 20–22 Aprel, 2017, p.32.

3. Electrical Conductivity – Frequency Dependence of nano silicon particles exposed to neutron irradiation, "Fizika və astronomiya problemləri" Beynəlxalq elmi konfransı, Bakı Dövlət Universiteti, Bakı, 25 may, 2018, s.225-228
4. Epithermal neutrons energy transfer process to nano-silicon, XII International Conference Nuclear and Radiation Physics, Institute of Nuclear Physics, Almaty, Kazakhstan, 24-27 June, 2019, p.60

Publications. Based on the materials of the thesis, 6 articles were published in high-rated foreign journals and 4 theses in materials of international conferences, 2 articles in republican journals.

Structure, scope and main content of the thesis. The dissertation consists of an introduction, five chapters, results, and a list of 203 references, covering the relevance of the work, goals, objectives, and other issues. The thesis consists of 218 printed pages, 39 figures and 10 tables of results.

The introduction substantiates the importance and relevance of the topic of the dissertation, both from a scientific and from a practical point of view. The introductory part contains the purpose of the dissertation and a list of research tasks aimed at achieving the goal, the novelty and practical significance of the results obtained, the main provisions for defense, approbation and information about publications.

The first chapter summarizes the existing literature data on the main topic of the dissertation. First of all, there are presented the distinctive properties of nanoscale materials, including silicon, size effects, their difference from bulk crystals. Materials on the effect of ionizing radiation and neutrons on nanoscale materials, including nano-silicon, as well as on the mechanism of interaction of neutrons with nuclei are analyzed. Information on electron spin resonance, Fourier-IR spectrometry, X-ray diffraction, electrical conductivity, dielectric constant and other methods used in the study of the structure, dimensions, defect states, electrical properties of nanosized materials and the results obtained on their basis are presented. Based on the analysis of the literature review, a generalization is made, and the formulation of the topic of the thesis is justified.

The second chapter presents the methodology of research carried out on the topic of the dissertation. First of all, information was provided about the research object, its manufacturer, composition, particle size and other physical properties. Irradiation of nano-silicon with neutrons was carried out at the Slovenian research nuclear reactor TRIGA Mark II. After irradiation of the samples in the central channel A1 of the reactor with a fluence of $6.912 \cdot 10^{16} \div 1.382 \cdot 10^{18}\, neutron/cm^2$ for $190 - 200\, hours$ in the Ortec HPGe and Canberra Coaxial HPGe detectors, the activity, the energy of the emitted radiation and the decay kinetics were studied. On the basis of the results obtained, the energies and radiation doses acting on nano-silicon during decay and, ultimately, the concentration of the existing nuclei of the main and mixed elements were determined. The structural composition of nano-silicon and the effect of neutron irradiation on these constituent fragments were studied by Fourier IR-spectroscopy. Fourier transform IR absorption spectra were measured on a Varion 640 FT-IR spectrometer in the frequency range $\nu = 4000 \div 400\, cm^{-1}$. For this purpose, tablets with a thickness of $50 - 100\, \mu m$ were prepared in a special mold. IR-spectra were recorded in special quartz cuvettes with CaF_2 window. The observed absorption bands were identified on the basis of literature data.

The electrical conductivity and dielectric constant of non-irradiated and irradiated nano-silicon samples were studied at the Josef Stefan Institute in Slovenia using the Novocontrol Alpa High Resolution Dielectric Analyzer and a Hewlett Packard 4284 A sensitive LGR-meter. For this, in the Laboratory of Physics of Thin Films and Surfaces of the Joseph Stephan Institute under special conditions nano-silicon tablets with a height of $250\, \mu m$ and a diameter of $5\, mm$ were prepared by compressing the powder under a pressure of $3\, kN/cm^2$. Then the tablets were irradiated with neutrons at a flux density of $\sim 1.92 \cdot 10^{13} neutron/cm^2 \cdot s$ in the central channel of the TRIGA MARK II reactor for 1, 5, 10, 20 hours. Due to the radioactive isotopes formed during neutron irradiation, the radioactivity of the samples increases to $A \approx 3.1\ GBq$. After irradiation with neutrons to reduce the radioactivity to an acceptable level, the nano-silicon samples were stored for $\tau = 400\ hours$ in a special chamber. Then, silver contacts were applied to the surface of the samples under special conditions, and their quality was checked on the basis of microscopic studies (Oguessa, Leitsilber 200). Cr/Au electrodes were deposited on the upper layers of the samples. The electrical conductivity of the samples was measured by placing them between platinum plates. The studies were carried out in the Laboratory of "Ceramic Electronics" of the Josef Stefan Institute in Slovenia at frequencies of $1\ Hz - 1\ MHz$, in the $T = 100 \div 400K$ temperature range, with an accuracy of $10^{-6}Hz$ and $10^{-2}K$, accordingly.

The scanning electron microscope (SEM) method was used to study changes in the surface and particle size of nano-silicon irradiated with a neutron flux. For this, the initial and irradiated nano-silicon powders were placed on a measuring disk of a "ZESS SIGMA YP FE-SEM" scanning electron microscope and measurements were performed. The used SEM device had an additional attachment for X-ray Fluorometric Analysis, which allows studying the composition of the surface of the samples. Electron Spin Spectrometry has been used to study biographical and radiation-induced paramagnetic defects in nano-silicon. Neutron-irradiated and non-irradiated nano-silicon samples were examined on a Bruker ELEXSYS E500 ESR-spectrometer at the Condencad Matter Physics F5 laboratory at the Josef Stefan Institute in Slovenia.

The third chapter presents the results of a study of the interaction of epithermal neutrons with the nuclei of elements in nano-silicon, energy transfer and the formation of defects. In the range of neutron energies used for irradiation, interaction with nuclei containing in nano-silicon occurs mainly due to scattering and capture processes.

$$\sigma_{total} = \sigma_s + \sigma_{capture} \quad (1)$$

The macroscopic cross sections of the interaction processes, the concentration of each isotope in $1\,cm^3$ of nano-silicon and its microscopic cross section were determined.

$$\Sigma_i = \sigma_i \cdot n_i \tag{2}$$

On the basis of the values of the neutron flux $\Phi = 1.92 \cdot 10^{13} neutron/(cm^2 \cdot \mathrm{sec})$ and the values of the macroscopic cross section in the central channel of the research nuclear reactor, the number of collisions of the nucleus of each isotope with neutrons under radiation conditions was determined.

$$N = \phi \cdot \sigma \cdot n_i \tag{3}$$

The number of collisions of elastic scattering and radiative capture for the Si-28 isotope was determined from the values of microscopic cross sections for elastic scattering and radiative capture for the silicon core $\sigma_s = 1.7 \pm 0.3\ barn$, $\sigma_a = 0.13 \pm 0.3\ barn$ and the values of the maximum recoil energy transferred to the environment (E_{rec}). For neutrons with an energy of $625\ eV$, at each collision the recoil energy $E' = 0.05\ eV$ is transferred to nano-silicon, and for neutrons with an energy of $E_n = 0.1\ MeV$ the recoil energy $E'' = 7.9\ eV$ is transferred.

Taking into account the (E') and (E'') values of the neutron energies used in irradiation, the value of the total recoil energy ($\Sigma E'_{max}$) transferred to the medium as a result of elastic scattering was determined:

$$(\Sigma E'_{max}) = N_s \cdot (E' + E'') = 4.44 \cdot 10^{11} eV/cm^2 \cdot sec \qquad \text{`(4)}$$

The energy transferred per unit volume of nano-silicon at the maximum irradiation time $\tau = 20\ hours$ is

$$\Sigma E^- = \Sigma E'_{max} \cdot \tau_S = 3.2 \cdot 10^{16} eV/cm^3 \tag{5}$$

When neutrons interact with nuclei $^{28}_{14}Si$, $^{29}_{14}Si$, stable nuclei $^{29}_{14}Si$ and $^{30}_{14}Si$ are obtained, and when interacting with nuclei $^{30}_{14}Si$, an non-stable nucleus $^{31}_{14}Si$ is obtained. In this case, interaction occurs according to the following nuclear reaction:

$$^{30}_{14}Si(n,\gamma)^{31}_{14}Si \tag{6}$$

The gamma-quanta released as a result of this process interact with the electron shell of nano-silicon and transfer a certain amount of energy to the nano-Si structure. Under the experimental conditions, the maximum time of neutron irradiation is $\tau = 20\, hours$. Energy of $\Sigma E_\gamma = 9.85 \cdot 10^{18} eV/cm^3$ is transferred to nano-silicon by gamma- rays emitted by unstable nuclei $^{31}_{14}Si$ formed upon interaction with neutrons in the specified time interval. The radioactive nucleus $^{31}_{14}Si$ obtained by the nuclear reaction (6) undergoes beta decay according to the following scheme.

$$^{31}_{14}Si \xrightarrow{T_{1/2}=2.62\, hours} {}^{31}_{14}P + \beta + \bar{\nu} \tag{7}$$

where β is a beta particle with energy of $E_\beta = 0.595\, MeV$, $\bar{\nu}$- is antineutrino.

The amount of energy $\Sigma E_\beta = 4.63 \cdot 10^{18} eV/cm^3$ is spent on the processes of ionization of the environment by beta-particles, which are the product of the β-decay of radioactive nuclei formed as a result of irradiation with neutrons for $\tau = 20\, hours$.

With the help of gamma-spectrometry, the main and impurity nuclei were identified when exposed to the nano-Si sample, which is the object of the study, the energy of the emitted rays and the kinetics of radioactive decay processes were investigated.

The amount of energy transferred into the environment by the nuclei observed in neutron-activated nano-Si in the form of an impurity by means of gamma rays was estimated as a result of the process

$$ {}_{x}^{Y}A(n,\gamma)^{y+1}_{X}A \quad (8) $$

$$ \sum_{mix} E_{\gamma} = 3.29 \cdot 10^{18} eV/cm^3 \quad (9) $$

In general, as a result of the processes of elastic scattering and radiative capture under the action of epithermal neutrons on the studied nano-Si samples, an amount of energy can be transferred to nano-Si

$$ \sum_i E_i = \sum_S E_S + \sum_{\gamma} E_{\gamma} + \sum_{\beta} E_{\beta} + \sum_{\gamma} E_{mix}. \quad (10) $$

Here $\sum_S E_S$ is the recoil energy during scattering, $\sum_{\gamma} E_{\gamma}$ is the energy released during a nuclear reaction ${}^{31}_{14}Si(n,\gamma){}^{31}_{14}Si$, $\sum_{\beta} E_{\beta}$ is beta released during radioactive decay, $\sum_{\gamma} E_{mixture}$ is the energy released into the environment by mixed nuclei in nano-Si as a result of neutron activation processes. If we substitute the values of their specific energies, we can estimate the total energy given off by nano-Si when it is irradiated for 20 hours.

$$ \sum_i E_i = 1.78 \cdot 10^{19} eV/cm^3 \quad (11) $$

Limiting energies of formation of electron-hole pairs in semiconductors

$$ E_h = 3 \cdot E_g \quad (12) $$

Considering that for nano-silicon samples $E_g = 1.55\, eV$, it is possible to estimate the number of electron-hole pairs that can form upon irradiation of n-Si with neutrons for 20 hours:

$$ N_{pair} = \frac{\sum_i E_i}{E_h} = 3.8 \cdot 10^{18} pair/cm^3 \quad (13) $$

In our experiments, we studied the kinetics of radioactive decay processes during $\tau = 360\, hours$ after irradiation of nano-silicon with neutrons. It was found that the radioactivity of radioactive nuclei formed by irradiation of nano-silicon with neutrons varies from $A = 0.1\ kBq$ to $A = 3.1\ GBq$, and the half-life varies in a wide range from $T_{1/2} = 2.2\ minute$ to $T_{1/2} = 5.3\ year$. We conditionally divided radioactive nuclei detected by gamma spectrometry into five groups depending on their activity and lifetime. I- $A \leq 3.5\ kBq$; II- $A \leq 35\ kBq$, III- $A \leq 3.1\ GBq$; IV- $A \leq 30\ MBq$; V- $A \leq 350\ kBq$. Experimentally, group I includes 12 isotopes $La-40$, $Sc-47$, $Ba-131$, $H-181$, $Fe-50$, $Sb-124$, $Co-58$, $Sc-46$, $Zn-65$, $Mn-54$, $Cd-109$ and $Co-60$. The second group includes three isotopes $W-187$, $Br-82$, $Sb-122$. The third group includes two isotopes $Cu-64$, $Cr-51$, the fourth group - three isotopes $Cl-35$, $Mn-65$, $Si-31$, and the fifth group - two isotopes $V-52$, $Al-28$.

The fourth chapter presents the results of experimental studies of defects in nano-Si under the influence of epithermal neutrons by X-ray diffraction, Fourier-IR, electron spin spectroscopy and special SEM methods with an XRD-attachment.

The changes occurring in the structural ordering of nano-silicon upon irradiation with neutrons for $\tau = 1 \div 10$ hours were studied by the method of X-ray diffraction. It was found that, upon irradiation in the indicated range, a decrease in the line intensity is observed in the diffractogram of nano-silicon. Comparison with X-ray diffraction patterns of non-irradiated samples shows that, upon irradiation with epithermal neutrons for $\tau = 1 \div 10$ hours, amorphization occurs in nano-silicon by 35–38%. Fourier transform infrared spectrometry opens up more possibilities for studying the processes of defect formation in nano-silicon under irradiation with neutrons and changes in the structural and surface functional groups in the adsorption and chemisorption phases. The absorption bands observed in the Fourier-IR spectrum of nano-silicon can be divided into three characteristic parts. The first group of absorption bands is the absorption bands corresponding to lattice vibrations of nano-silicon, the second group is the lattice vibrations of the oxide phase, and the third region is the absorption bands of SiH_x, $\equiv Si-OH$ functional groups, adsorbed water and hydrocarbons. In the observed Fourier-IR spectra, $\nu = 479\ cm^{-1}$ correspond to bending vibrations in δSi bonds in the low-frequency region, multiphonon absorption $\nu = 610\ cm^{-1}$, corresponding to single-crystal silicon, $800\ cm^{-1}$ and intense wide $1075\ cm^{-1}$ correspond to symmetric and are asymmetric to vibrations in Si-O-Si bonds. It was found that upon contact of nano-silicon with air, an oxide layer is formed, for which the IR-absorption region corresponds to $1085\ cm^{-1}$. Asymmetric stretching vibrations (V_{as}) of internal Si-O-Si bonds are observed in Fourier-IR spectra as a doublet at $1161 - 1105\ cm^{-1}$. It is observed a band $\nu = 2000 - 2400\ cm^{-1}$, corresponding to the phase SiH_x, absorption bands in the region $\nu = 3100 - 3900\ cm^{-1}$, corresponding to molecularly and dissociatively adsorbed water molecules, different types of hydroxyl groups. It was found that the intensity of absorption bands in Fourier-IR-spectra, which qualitatively characterizes the change in the number of Si-O-Si, SiH_4 and Si-H_2O fragments under the action of neutrons on nano-silicon, depends on the irradiation time (Figure1).

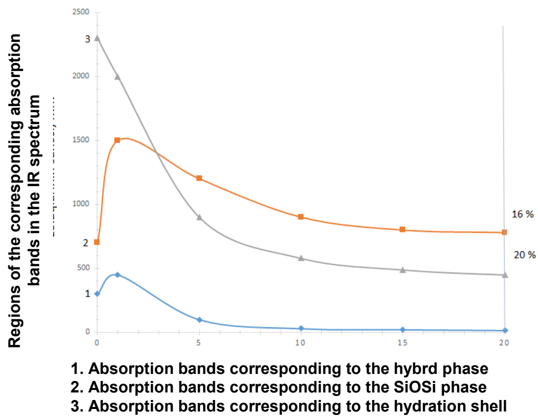

Fig. 1. Time dependence of irradiation of areas IR absorption of nano-silicon constituents - phases of oxide (Si O Si) (2), hydride SiH_x (1) and hydrate (3) under the effect of epithermal neutrons

Samples irradiated with epithermal neutrons were examined using a scanning electron microscope with a special analytical attachment. The results obtained show that as a result of irradiation, nano-silicon particles agglomerate, as a result of which the particle size increases by $1.5 \div 4$ times. The formation of oxygen-containing silicon compounds in silicon nanoparticles upon irradiation by epithermal neutrons, along with Fourier-IR-spectroscopy, was also determined by investigation using an SEM with an XRD attachment. As a result of radiation processes, the amount of the oxygen phase increases by about 16.6%, which corresponds to an increase in absorption lines corresponding to Si-O-Si bridging bonds observed in FourierIR-absorption spectra.

Fourier transform infrared spectroscopy and SEM studies show that non-irradiated nano-silicon contains oxygen-containing silicon compounds. Therefore, in the initial samples ESR spectral lines are observed in the region of the g-factors corresponding to $\equiv Si$,$\equiv SiO$ radicals characteristic of oxygen-containing compounds of ordinary silicon.

In addition, the study of nano-silicon using neutron activation showed that it contains up to $\sim 1\%$ impurity of transition elements. Transition elements play the role of electroacceptor centers in the Si medium and are in an ionized state. These ionized cations are paramagnetic and their characteristic ESR lines are observed in the $g = 3.5 \div 5.0$ region. Electrons and holes formed in the environment as a result of ionization processes in silicon under irradiation with neutrons are localized on structural defects, and some of them are paramagnetic and are observed in the ESR spectra as electron L(n) and hole L(p) ($\equiv SiO^-$) centers in $g \sim 2.02$ and 2.10 regions, respectively. The free electrons formed during neutron irradiation are captured by the cations of transition elements and become non-paramagnetic, and no lines are observed in the ESR spectra in the region $g = 3.5 \div 5.0$ of their inherent factors.

The fifth chapter describes the results of a study of nuclear and radiation processes occurring in nano-silicon under the effect of epithermal neutrons and their effect on dielectric properties and electrical conductivity. The dependence of the real and imaginary parts of the electrical conductivity of nano-silicon, irradiated with neutrons in different doses, on frequency in the range of $1 \div 10^{16}\ Hz$ and on temperature in the $T = 100 \div 400K$ range has been investigated. It was found that both the real and the imaginary parts of the electrical conductivity of nano-silicon increase linearly with an increase in the neutron dose in the $D \approx 0 \div 1.38 \cdot 10^{18} neutron/cm^2$ range. Chaos was found in the frequency dependence of the real part of the electrical conductivity both in non-irradiated and irradiated with neutrons in the studied dose range of nano-silicon samples at $T \leq 300\,K$ temperatures.The observed randomness decreases with increasing temperature and disappears at $T = 400K$.

It was found that the real part of the electrical conductivity at low temperatures $T \leq 300\,K$ in the first frequency range depends weakly on temperature. A sharp increase is observed in the next temperature range. This growth is more dramatic with an increase in the neutron irradiation dose. The measurements showed that with an increase in the frequency of the electric field, the effect of the radiation dose on the temperature dependence of the real part of the electrical conductivity becomes stronger.

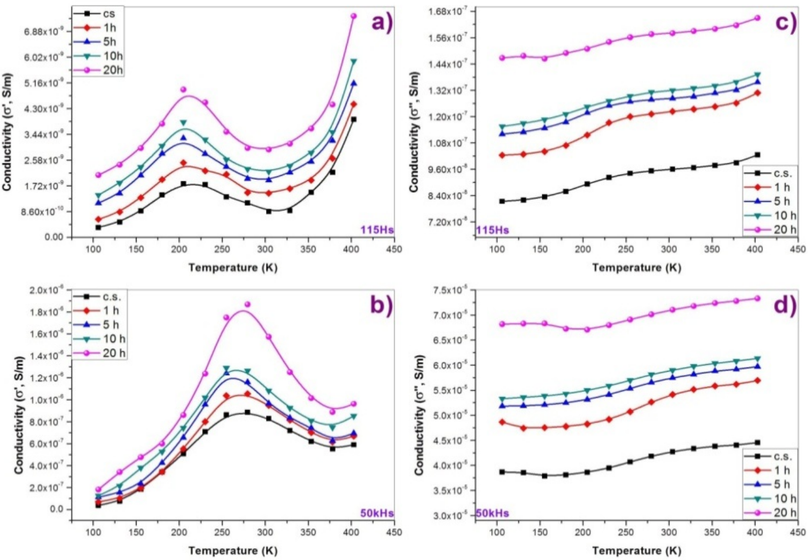

Fig. 2. Temperature dependences of the real (a and b) and imaginary (c and d) parts of the electrical conductivity of nano-silicon in its original state (c.s.) and exposed neutron flux for different times (1, 5, 10, 20 hours) at different frequencies in the midrange

On the temperature dependence of the real part of the electrical conductivity of non-irradiated and neutron-irradiated nano-silicon, a maximum is observed, which changes its location and intensity with increasing frequency. Thus, the maximum observed at frequencies of $1 \div 10\ Hz$ at $T = 170K$ is shifted to $T = 320K$ at a frequency of $1\ MHz$. With increasing frequency, the intensity of the observed maximum in the temperature dependence of electrical conductivity increases.

With increasing frequency, the effect of temperature on the imaginary part of electrical conductivity becomes less pronounced. On the basis of the temperature dependence of the electrical conductivity in Arrhenius coordinates $ln\sigma = f(\frac{1}{T})$, the activation energies of the conductivity were determined at different frequencies and values of neutron irradiation doses. The temperature dependences of the real part of the electrical conductivity in Arrhenius coordinates at different frequencies for the initial and irradiated samples mainly consist of three parts. In nano-silicon, the activation energy of electrical conductivity decreases with an increase in the radiation dose and the frequency of the electric field. The observed activation energies change in the $E_{ac} = 0.01 \div 3.6\ eV$ region. The identified three areas can be conditionally divided into areas of low, medium and high temperatures. The activation energy of conduction observed at high temperatures varies in the range of $E_1 = 0.5 \div 3.5\ eV$, in the range of $E_2 = 0.12 \div 0.82\ eV$ at medium temperatures and in the range of $E_3 = 0.09 \div 0.74\ eV$ at low temperatures. The decrease in the activation energy of the electrical conductivity of nano-silicon with an increase in the irradiation dose is explained by the relatively shallow capture levels formed as a result of radiation processes and the high free energy of charge carriers.

The effect of neutron irradiation on the real and imaginary parts of the dielectric constant in nano-silicon was studied in the $100 \div 400K$ temperature range, $\nu \approx 1 \div 10^6 Hz$ frequency range, and at values $F = 6.91 \cdot 10^{16} \div 1.38 \cdot 10^{18}\ neutron/sm^2$ neutron flux. It was found that the frequency dependence of the imaginary part of the dielectric constant in the region of low $f_a \geq 10^5 Hz$ and high frequencies $f_y \geq 10^{13} Hz$ is chaotic, which can be explained by the presence of clusters or resonance processes in the system. At low temperatures ($T \approx 100$ K), the real part of the dielectric constant is practically independent on frequency. The real part of the dielectric constant of nano-silicon in all studied ranges of temperatures and frequencies increases with growth in the radiation dose.

Below, using the example of ($115\, Hz - 50\, kHz$) medium frequencies, the effect of the radiation dose on the temperature dependence of the real ε' and ε'' imaginary parts of the dielectric constant is shown (Fig.3).

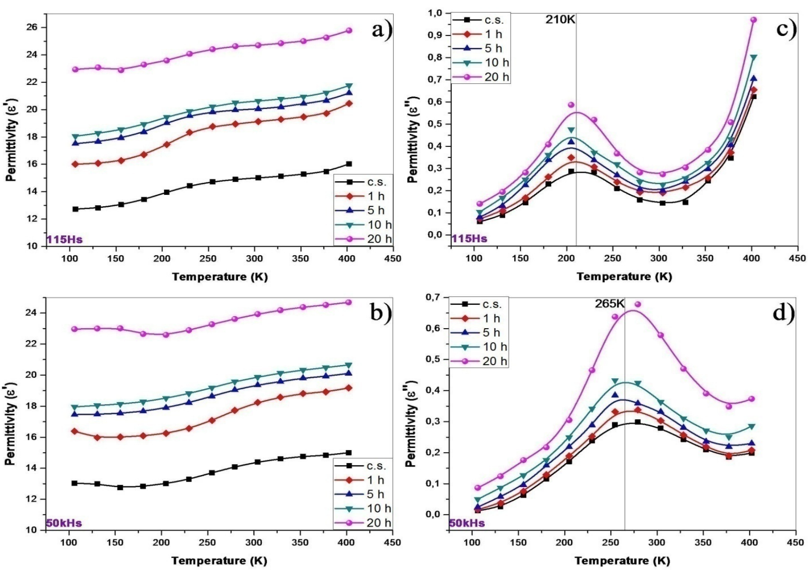

Fig.3. Effect of neutron irradiation on temperature dependence of real ε' (a), (b) and imaginary ε'' (c), (d) parts of the dielectric constant at low and mid frequencies

On the temperature dependence of the imaginary part of the dielectric constant, maximum $T_{max} \sim 117 \div 315\, K$ is also observed, as on the temperature dependence of the real part of the electrical conductivity, which increases with increasing frequency and shifts towards high temperatures.

The isofrequency and isotemperature cross sections of the frequency and temperature dependences of the real and imaginary parts of the dielectric constant of the samples irradiated with neutrons at different doses show that with an increase in the neutron irradiation dose, both components of the dielectric constant of nano-silicon grow.This increase indicates that neutron ionization processes increase the polarization in the sample.

The mutuality of the real and imaginary parts of the dielectric permittivity $\varepsilon'' = f(\varepsilon')$ of nano-silicon under the effect of different neutron fluxes in the $T = 100 \div 400K$ temperature range was investigated. These dependences exhibit strong randomness at low temperatures. At relatively high temperatures, a situation similar to the Cole-Cole diagram is observed. Relaxation times can be calculated from the imaginary continuation of these curves. The relaxation times determined from the observed curves vary over a very wide range of $\sim 10^{-3} \div 10^{-10}$ seconds.

On the basis of the obtained relaxation times, a judgment on the nature and mechanism of polarization in the nano-silicon samples is advanced. Based on the frequencies corresponding to the observed relaxation time, one can reason about the presence in nano-silicon of atomic, dipolar polarization or polarization of surface charges.

Establishing of the fact, that which part of the charge carriers $N_{pair} = 3.8 \cdot 10^{18}\, pair/cm^3$, forming due to the energy $\sum_i E_i = 1.78 \cdot 10^{19}\, \mathrm{eV/cm^3}$ transferred to the medium as a result of elastic scattering, radiation capture and radioactive decay of unstable nuclei, arising from the action of neutrons on nano-silicon, is involved in electrical conductivity is of scientific and practical importance for solid state physics, radiation and nuclear physics, radiation materials science and other areas.

Theoretical calculations have shown that the concentration of non-equilibrium charge carriers observed in neutron-irradiated nano-silicon is much higher than the density of intrinsic charge carriers

($N_m = 1.5 \cdot 10^{10}$ particles$/cm^3$), which is characteristic for silicon-containing materials. Taking into account the processes occurring in nano-silicon under the action of neutrons, the designated free carriers undergo recombination and localization processes. Since the electrical conductivity of the irradiated samples is investigated within $\tau = 400$ hours after irradiation, only localized particles are involved in these processes. When measuring electrical conductivity, carriers located at different energy levels are released under the effect of the temperature and frequency of the electric field. From the temperature dependence of the electrical conductivity in nano-silicon, the presence of mainly three types of sufficiently deep levels was revealed. In order to calculate the concentration of charge carriers participating in the conductivity on the basis of the dose dependence of electrical conductivity, the charge and mobility of charge carriers must be known.

$$\sigma = q \cdot n \cdot \mu \qquad (15)$$

The concentration of charge carriers involved in a certain electrical conductivity varies in the range of $N_{el} = 1.45 \cdot 10^8 \div 1.64 \cdot 10^{13} cm^{-3}$. Comparison of the concentrations of initially formed and participating in the conductivity of charge carriers shows that

$$N_{el}/N_0 = \frac{1.64 \cdot 10^{13}}{3.18 \cdot 10^{18}} = 4.31 \cdot 10^{-6}, \qquad (16)$$

that is, only $\sim 10^{-6}$ part of them participates in electrical conductivity. The rest of the charge carriers undergo various types of recombination processes.

On the basis of a comparative analysis of the obtained theoretical and experimental results, explanations and mechanisms of the processes occurring in nano-silicon under the influence of neutrons and changes, revealed changes in physical properties are given.

MAIN RESULTS

Nuclear-neutron interactions in nano-silicon under the influence of neutrons with energy of $E_n = 625 \div 1 \cdot 10^5 eV$ and flux density of $\Phi = 1.29 \cdot 10^{13}\ neutron/cm^2$ ·have been studied, the processes of defect formation in nano-Si due to the energy transferred as a result of radiation capture and radioactive decay, and their effect on the physical properties of nano-silicon have been studied. Based on the results obtained, the following main conclusions can be drawn:

1. The main parameters of the interaction of neutrons with energy of $625 \div 1 \cdot 10^5 eV$ with the nuclei of natural isotopes $^{28}_{14}Si$, $^{29}_{14}Si$, $^{30}_{14}Si$ contained in nano-silicon, the rate of elastic scattering, radiation capture and formation of radioactive nuclei $^{30}_{14}Si$ have been determined. The energy transferred to nano-silicon by radiation resulting from elastic scattering, radiation capture and radioactive decay has been determined. The rate of formation of electron-hole pairs (n, p), which can be formed as a result of the ionization process in nano-Si due to these energies, and their concentration $Ns = 3.8 \cdot 10^{18}\ cm^{-3}$ at the maximum radiation dose $\Phi = 1.382 \cdot 10^{18} neutron/cm^2$ was determined.

2. The radiation of radioactive nuclei formed as a result of the interaction of basic silicon and mixed nuclei in the composition of nano-silicon with neutrons by the mechanism of radiation capture has been discovered, their energies and kinetic regularities of radioactive decay processes have been determined. Based on the activity of radioactive nuclei, their concentrations was determined with high accuracy. As a result of the studies carried out, the possibility of introducing $^{31}_{15}P$ atoms into the composition of nano-silicon by radiation doping was revealed.

3. The surface mobility and chemical activity of nano-silicon particles increase under the influence of neutrons, the particle size increases $1.5 \div 4$ times as a result of these processes. In non-irradiated nano-Si, paramagnetic centers of an electron-hole nature, specific for transition elements were identified. As a result of the localization of non-equilibrium charge carriers formed under the

influence of neutron radiation, the concentration of paramagnetic defects of an electron-hole nature sharply increases. Since transition elements are electron acceptors, capturing free electrons formed under the influence of radiation, they become non-paramagnetic. It was found that upon irradiation of nano-silicon with a neutron flux $\Phi = 6.91 \cdot 10^{17}\ neutron/cm^2$, the resulting structural defects cause a decrease in the structural ordering of the samples by 35-38%.

4. Biographical structural fragments of nano-silicon and the effect of neutron irradiation on them have been investigated that non-irradiated nano-silicon consists of a silicon lattice, an oxide of the Si-O-Si type, SiH_x -hydride, a hydroxyl, and a hydrate coating bound to the surface in various forms. It was found that, under the action of neutrons, the hydride phase SiH_x completely decomposes upon irradiation with a dose of $\phi \geq 3.45 \cdot 10^{17} neutron/cm^2$. It was found that, under the influence of neutrons, the hydration coating completely disintegrates in the dose range of $\Phi \geq 3.45 \cdot 10^{17} neutron/cm^2$ and leaves stable structural hydroxyl groups on the surface, which make up 20% of the initial coating. In the early stages of neutron irradiation, the surface is rapidly oxidized in the dose range of $\Phi \leq 1.04 \cdot 10^{17} neytron/cm^2$, some of the oxide fragments decompose in the dose range of $\Phi \leq 1.04 \cdot 10^{17} \div 6.912 \cdot 10^{17}\ neutron/cm^2$, and a more than $\sim$16% radiation-resistant oxide phase remains in comparison with non-irradiated samples. The formation of an oxide phase in nano-silicon and its growth by 16% as a result of irradiation was also confirmed by SEM-XRD.

5. Non-equilibrium charge carriers formed in nano-silicon as a result of nuclear and radiation processes under the effect of neutrons are localized at special levels, and under appropriate conditions - electric field frequency and temperature, overcoming the barriers of localization levels they participate in electrical conductivity. As a result, neutron irradiation creates a linear increase in the electrical conductivity of nano-silicon It was found that in nano-silicon charge carriers are mainly localized at three types of levels, the activation energies for these levels decrease with an increase in the frequency and dose of radiation.

6. Based on the values of the electrical conductivity of nano-silicon irradiated with neutrons, the mobility of carriers in silicon-containing materials, an approximate estimate of the concentration of carriers involved in electrical conductivity ($N_{el} \sim 1.45 \cdot 10^{8} \div 1.64 \cdot 10^{13}\ cm^{-3}$) was made. Studies have shown that only a part of the charge carriers formed under the action of neutrons on nano-silicon is involved in electrical conductivity. The rest of the charge carriers recombine or become non-electrically active. This result is of great importance in nuclear, aerospace, and radiation materials science for silicon-based materials.

7. As a result of polarization caused by nuclear and radiation processes during neutron irradiation, the dielectric constant of nano-silicon increases in real and imaginary parts depending on the radiation dose. These dependences, explanations of the observed effects, the nature and mechanism of polarization in n-Si as a result of irradiation are presented.

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Address: AZ1073, Qobu settlement, Baku-Shamakhi highway

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