Energy transfer and defect formation processes in nano silicon under the influence of epithermal neutrons

A. Garibli
National Nuclear Research Center, Baku, Azerbaijan
E-mail: qaribliaydan@gmail.com

The neutrons scattering and capture cross-section processes has been calculated for natural $^{28}\text{Si}$, $^{29}\text{Si}$, $^{30}\text{Si}$ isotopes which are main part of nanosilicon samples when irradiated for 20 hours by epithermal neutron flux. The values of energies has been determined which given to nanosilicon nuclei as a result of scattering processes in the energy intervals of investigated neutrons. The cross-sections of radiation capture process and the amount of $^{31}\text{Si}$ radioactive isotope which can be formed by by $^{30}\text{Si}$ isotope in the energy interval of epithermal neutrons, the parameters of energy supply and ionization processes has been determined by interaction between energy carried of $\beta$ - particles which disseminated in environment and silicon atoms as a result of their $\beta$ - decay. The formed defects has been determined in electron structure of nanosilicon under the influence of primary and secondary electron beams. Characterized interaction processes between nanosilicon and gamma rays irradiated from radioactive isotopes in impurities up to 1% in nanosilicon which formed under the influence of neutron flux. As a result of SEM investigation, interaction between surface defects inherent to nanoscale systems and $\text{O}_2$, $\text{H}_2\text{O}$ active components that arranged environment and increasing number of surface oxidation atoms determined under the influence of radiation from radioactive isotopes which are product of radiation capture processes when impact by neutron flux. The progression of agglomeration processes of nanosilicon particles under the influence of secondary radiation processes that caused by neutron flux has also been proved experimentally by SEM investigations. The characteristic of identification and generation processes of paramagnetic defects, that formed as a result of secondary radiation processes investigated by electron paramagnetic resonance spectroscopy method.

Keywords: neutrons scattering, capture cross-section, electron paramagnetic resonance spectroscopy.

Introduction

Therefore, nanomaterials is of great importance as an effective systems characterized with energy carrying, defect and the emergence of electron excitation factors.
and transmission to surface level. An example of such systems are nuclear fuel materials, high energy radiation detection systems, radiation catalysts and other processes related to radiation material science. In recent years, nano-matter and materials are widely applied as an actual and perspective systems for nuclear and radiation technologies according to these features.

Recently, nanosilicon attracting great attention from world scientists and some properties of this matter studied theoretically and experimentally [1-7]. Nano Si also has a wide range of application areas as electronics materials, particularly in space electronics and nuclear technologies [8-14]. Thus, nano Si which used in presented work are widely applied in nuclear and space technologies in micro sizes and their application areas are intended in nano level in the future.

The main purposes of the presented work are detection and characterization energy transmission, mechanism of radiation defect formation processes, defects identifications and quantitative characteristics, the changes on dimensions and surfaces of nanoparticles taking into account scientific and practical significance processes occurring in nano sized silicon under the influence of epithermal neutrons. For this purpose, has been detected scattering and radiation capture cross-sections of epithermal neutrons by nano Si and its constituent isotopes, possible options of defect formation processes and energy transmission considering decay processes of formed radioactive isotopes [15-28]. The volume and surface properties of nano size materials and changing of surface composition and particle sizes as a result of radiation processes investigated by SEM method. Localized states in different structure and composition defects of non-equilibrium charge carriers and in most cases different defects have paramagnetic properties. Therefore, defect formation processes investigating by EPR method [29-40]. That is, we have been investigated defect formation processes in nano silicon samples under the influence of epithermal neutrons by EPR spectroscopy method.

**Experiments**

Nanomaterial used in the experiment is cubic silicon nano particles which have specific surface area of 80 m²/g, measure particles of 100 nm and density of 0.08 g/cm³. [production company: SkySpring Nanomaterials, Inc. Houston, USA]. Nano silicon were irradiated with neutron flux density of 2 × 10¹³ n/cm² s in full power (250 kVt) in the channel A1 of Trig Mark II light water pool type research reactor in the "Reactor Center" of Jozef Stefan Institute in Ljubljana, Slovenia. Neutron flux has the following integral part when reactor is running in full power [24-26]: flux density for thermal neutrons is 5.107 × 10¹² n/cm² s (1 ± 0.0008, \( E_n <625 \) eV), for epithermal neutrons is 6.502 × 10¹² n/cm² s (1 ± 0.0008, \( E_n \approx 625 \) eV ÷ 0.1 MeV), for fast neutrons is 7.585 × 10¹² n/cm² s (1 ± 0.0007, \( E_n >0.1 \) MeV), and finally for all neutrons is like 1.920 × 10¹³ n/cm² s (1 ± 0.0005) in the channel A1. As a result, the average energy of neutrons in the channel can be characterized as energy of epithermal neutrons which is equal to \( E_n \approx 625 \) eV ÷ 0.1 MeV.

SEM analyzes carried out by “ZEISS SIGMA VP FE-SEM” device for up to 20 hours irradiated samples by neutron. Each of the 20 hours irradiated and primary
samples filled with 5 mg in high purity cylindrical quartz ampules with 5 mm height and 2.5 mm internal diameter. EPR analyzes of the primary and irradiated samples carried out by “Bruker ELEXSYS E500 EPR spectrometer with high-Q resonator” device at Jozef Stefan Institute. EPR spectra of primary and irradiated nano Si has been measured with two cases: “wide range” and “selected range”.

Results and discussions

It’s known that, the silicon elements have three natural isotopes: $^{28}\text{Si}$ (92.2%), $^{29}\text{Si}$ (4.7%) and $^{30}\text{Si}$ (3.1%) [16]. The amount of irradiated isotopes of sample in a unit volume determined as follow [15, 19]:

$$n = \frac{\rho}{A} N_A,$$  

(1)

The scattering and capture processes can occurs during an interaction between epithermal neutrons and silicon atoms:

$$\sigma_z = \sigma_s + \sigma_{r,\text{tutma}} + \sigma_f,$$  

(2)

The macroscopic cross-section of general scattering and capture processes has been appointed based on the microscopic cross section of our samples and survey materials [15, 17, 18] without considering the isotope composition of the silicon element. Firstly, the number of collisions per unit time has been determined based on $\phi=1.92 \times 10^{13}$ neutron/cm$^2$ - the value of given neutron flux and the number of nano silicon atoms in 1 cm$^3$ volume ($n=1.7 \times 10^{21}$) which appointed by formula (1).

$$N = \phi \cdot \sigma \cdot n,$$  

(3)

In the condition of our experiment the number of collision can be determined by formula (3) based on both mechanism in a unit time by using $\sigma_s = 1.7 \pm 0.3$ barn, $\sigma_a = 0.13 \pm 0.03$ barn values of microscopic cross-section both for general scattering and absorption from literature.

$$N_{\text{scat.}} = 1.92 \times 10^{13} \text{ neutron/cm}^2 \cdot \text{s} \cdot 1.7 \times 10^{-24} \cdot \text{cm}^2 \cdot 1.171 \times 10^{21} \text{ atom/cm}^3 =$$

$$= 5.58 \times 10^{10} \text{ collision (neutron \cdot atom/cm}^3 \cdot \text{s)},$$  

(4)

$$N_{\text{capt.}} = 1.92 \times 10^{13} \text{ neutron/cm}^2 \cdot \text{s} \cdot 0.13 \times 10^{24} \cdot \text{cm}^2 \cdot 1.71 \times 10^{21} \text{ atom/cm}^3 =$$

$$= 0.819 \times 10^{10} \text{ neutron \cdot atom/cm}^3 \cdot \text{s},$$  

(5)

Thus, in the process of interaction between epithermal neutrons and natural silicon there are $5.58 \times 10^{10}$ scattering and $0.819 \times 10^{10}$ capture processes occurs in a unit time and volume.
Apparently, elastic scattering prevails. Therefore, during the scattering we can calculate given energy to nano silicon according to starting and ending points of energy interval of epithermal neutrons [19]:

\[ E_{\text{max}} = 4A \cdot E_n \cdot \cos^2\phi / (1 + A^2), \] (6)

in here,

\[ E_n = 625 \text{ eV}; \cos\phi = 0.024; E'_{\text{max}} = 0.05 \text{ eV}, \] (7)

In case of 0.1 MeV energy of epithermal neutrons \( E''_{\text{max}} = 7.9 \text{ eV} \) energy transferred to silicon core for each collisions with silicon. These energies insufficient for nuclear excitation processes because can procreate ionization and excitation processes in electron structure of atom.

\[
\text{Nano Si} \rightarrow n + p + \text{Si}^*, \quad (8)
\]
in here, \( n \) – electron, \( p \) – hole, \( \text{Si}^* \) - defect cases in excited and other featured.

And now we can determine the number of atoms in 1 cm\(^3\) of each isotope based on the amount of interest considering the isotopic composition of silicon irradiated by neutrons.

\[
n_{28\text{Si}} = 1.56 \cdot 10^{21} \text{ atom/cm}^3; n_{29\text{Si}} = 7.9 \cdot 10^{19} \text{ atom/cm}^3; n_{30\text{Si}} = 5.1 \cdot 10^{19} \text{ atom/cm}^3, \quad (9)
\]

Mainly radiation capture processes of neutrons are occurred with interaction neutrons on the isotopes side.

\[
^{28}\text{Si} + n \rightarrow ^{29}\text{Si}, \quad (10)
\]

\[
^{29}\text{Si} + n \rightarrow ^{30}\text{Si}, \quad (11)
\]

\[
^{30}\text{Si} + n \rightarrow ^{31}\text{Si}, \quad (12)
\]

The stable \(^{29}\text{Si}\) and \(^{30}\text{Si}\) cores obtained as a result of (10, 11) processes. And \( \beta \) radioactive \(^{31}\text{Si}\) core formed as a result of (12) process. Macroscopic cross-section of neutron capture processes for mentioned processes can be described as follow:

\[
\Sigma_a = \sigma_a \cdot n, \quad (13)
\]

In here, \( \sigma_a \) – microscopic cross-section of absorption processes of neutrons by corresponding isotopes, \( n \) – number of isotope nucleus in 1 cm\(^3\).

\[
\sigma_a(^{28}\text{Si}) = 80 \cdot 10^{-3} \text{ barn},
\]

\[
\sigma_a(^{29}\text{Si}) = 0.27 \text{ barn},
\]

\[
\sigma_a(^{30}\text{Si}) = 0.41 \text{ barn},
\]

\[
\Sigma_n(^{28}\text{Si}) = 1.25 \cdot 10^{-4} \text{ 1/cm},
\]
\[ \Sigma_{a}(^{29}\text{Si}) = 2.13 \cdot 10^{-5} \text{ 1/cm}, \]
\[ \Sigma_{a}(^{30}\text{Si}) = 2.09 \cdot 10^{-5} \text{ 1/cm}, \] (14)

We can determine number of collision by formula (3) based on neutron capture mechanism of epithermal neutrons with relevant isotopes

\[ N_{^{28}\text{Si}} = 2.4 \cdot 10^{9} \text{ neutron \cdot atom/cm}^3 \cdot \text{s}, \]
\[ N_{^{29}\text{Si}} = 4.09 \cdot 10^{8} \text{ neutron \cdot atom/cm}^3 \cdot \text{s}, \]
\[ N_{^{30}\text{Si}} = 4.01 \cdot 10^{8} \text{ neutron \cdot atom/cm}^3 \cdot \text{s}, \] (15)

As can be seen the probability of scattering is more likely in the interaction processes between epithermal neutrons and natural isotopes of silicon.

The maximum energy that can be given to sample during an elastic scattering in a unit time.

\[ \Sigma_{E_{\text{max}}} = N_{\text{scatt.}} \cdot (E' + E'') = 5.58 \cdot 10^{10} \times 7.95 \text{ eV} = 4.44 \cdot 10^{11} \text{ eV/cm}^3 \cdot \text{s}, \] (16)

Thus, \( 4.44 \cdot 10^{11} \text{ eV} \) energy is given in a unit time and volume only by elastic scattering when Si irradiated with epithermal neutrons. Irradiating time is \( \tau = 20 \) hours, in this case:

\[ \Sigma_{E_{\text{max}}} \cdot \Delta t = 4.44 \cdot \frac{10^{11} \text{ eV}}{\text{sm}^3} \cdot \text{s} \cdot (20 \cdot 60 \cdot 60) \text{ s} = 3.2 \cdot 10^{16} \text{ eV/cm}^3, \] (17)

The \( ^{31}\text{Si} \) isotope which formed by above-mentioned (12) process is unstable and exposing to \( \beta^- \) decay.

\[ ^{31}\text{Si} T_{1/2} = 2.62 \text{ hours} \rightarrow ^{31}\text{P} + \beta^- + \bar{\nu}, \] (18)

In here, \( \beta^- \) – beta particle, \( \nu \) – antineutrino.

The energy of \( \beta^- \) particles is \( E_\beta = 1.266 \text{ MeV} \) [16] and interacting with electron structure of Si atoms. The beta rays can lose energy as radiation and ionization energy in the nano Si environment. The energies of the formed beta particles are \( E_\beta > m c^2 \) because may be considered relativistic electron in nano Si.

The probability of energy loss of \( \beta^- \) particles which formed as a result of radioactive decay of \( ^{31}\text{Si} \) isotopes is more likely generating brake beams and ionization [17-19]. If we accept the energy of beta particles with MeV, than the ratio of losses of energy [15, 19] to irradiation \( (-dE/dx)_{\text{irrad.}} \) and ionization \( (-dE/dx)_{\text{ion.}} \) processes during dissemination in environment can be describe in the simplified form as follow:

\[ \frac{(dE/dx)_{\text{irrad.}}}{(dE/dx)_{\text{ion.}}} = \frac{E_e \cdot Z}{800}, \] (19)

If we put the values of energy of \( \beta^- \) - rays and \( Z \) to places, then contrast ratio equal to:

\[ \frac{(dE/dx)_{\text{ion.}}}{(dE/dx)_{\text{irrad.}}} = 45, \] (20)
That is, $\beta$-particles which are the product of $^{31}$Si beta decay mainly losses energy as a result of ionization processes in silicon environment. If we take $4 \cdot 10^8$ atom/cm$^3$·s for acquisition speed of $^{31}$Si isotope, the number collected $^{31}$P samples during $\tau = 20$ hours are: $\Delta N = \omega \cdot \Delta t = 7.2 \cdot 10^4 \cdot 4.01 \cdot 10^8 = 2.85 \cdot 10^{13}$ atom/sm$^3$. The total energy of beta radiation:

$$E_{rad} = E_\beta \cdot N_\beta = 3.62 \cdot 10^{19},$$

(21)

The parts of the energy ($E_{rad}$) of $\beta$-particles spent to $8 \cdot 10^{17}$ eV – electromagnetic beams and $3.54 \cdot 10^{19}$ eV to ionization. Nano silicon is a semiconductor materials and band gap is $E_g = 1.55$ eV [20].

The limit energy of ionization processes in semiconductors determined as follow [20]:

$$E_{lim} = 3.0E_g,$$

(22)

In here, $E_{lim}$ – limit energy, $E_g$ - band gap.

The number of ionization processes committed by $\beta$-rays which formed as a result of radiation capture and $^{31}$Si decay under the influence of epithermal neutrons of nano silicon can be characterized. For Si, $E_h = 3.0$ eV and $E_g = 4.65$ eV.

$$N_{ion} = \frac{E_{rad}}{E_h} = \frac{3.62 \cdot 10^{19} \text{eV/cm}^3}{4.65 \text{eV}} = 0.78 \cdot 10^{19} \text{1/cm}^3,$$

(23)

Thus, $7.8 \cdot 10^{18}$ ionization processes can occurs in per 1 cm$^3$ nano Si due to the formed beta rays from radioactive $^{31}$Si decay as a result of radiation capture of the main material of $^{30}$Si under the influence of epithermal neutrons. The investigated nano Si has 99% purity and 1% other impurities (values according to a manufacturer) and the majority of these impurities tend to radiation capture of epithermal neutrons. Ionization processes can occurs due to the irradiation as a result of decay of the formed radioactive nuclei. The results of the formed radioactive isotopes and their capture processes as a result of radiation capture processes in nano Si which investigated under the influence of epithermal neutrons given in [41]. Radioactivity of formed mixed isotopes between 0.1 kBk – 3.1 kBk and the energy of irradiated gamma rays is appropriate to $E_\gamma \approx 1.3$ MeV. The gamma rays with these energies mainly an interaction by compton scattering mechanism with electron composition of Si atoms [22-24]. As a result of this interaction can be generate $\delta$ electrons approximately range of $E \leq 1.0$ MeV. It losses the energies in silicon environment by appropriate mechanism to $\beta$ rays of the $^{31}$Si isotope.

The mechanism of $C_{^{31}Si} > C_{\text{admixture}}$ (1%) radiation defect formation processes which investigated according to natural isotope composition of nano Si explained an example of $^{31}$Si isotopes. Schematic description of ionization processes of Si nanoparticles in general:

$$n - Si \xrightarrow{\beta, \gamma, \delta-\text{electron}} n - Si^+ + e,$$

(24)
In here, Si\(^{+}\) - free holes, e\(^{-}\) - free electrons. If we consider that, the dimensions of investigated nano Si are \(d = 100\) nm, the length of –Si–Si– bond \(l_{\text{Si-Si}} = 0.163\) nm, the formed non-equilibrium carries by scheme (21) interacts with electron shells of silicon atoms by \((6-7) \cdot 10^2\) –Si–Si– bond and migrate by losing energy.

The braking of electrons with different energies in the silicon, investigated experimentally [21] and theoretically [22, 23]. It has been determined that, the dependence of energy losing from energy passes around from \(E_{\delta-e} = 10^2\) eV maximum and decrease by increasing energy [22-24]. For example, for the electrons with \(E_{\delta-E} = 20-30\) eV energy is \(-dE/dx \approx 10\) eV/nm; for \(E_{\delta-E} = 10^2 - 10^3\) eV is \(-dE/dx \approx 10^2 - 20\) eV/nm and for \(E_{\delta-E} > 10^5\) eV is \(-dE/dx \approx 1\) eV/nm [22-24].

That is, the formed \(\delta\) electrons in our investigations only can overcome \(R = 100\) nm of nano Si particle size only with \(E_{\delta-e} > 10^3\) eV energy. The low energy electrons localized in defect structures and mixed atoms with losing energy in nano Si particles. So, occurs the oxidation processes of surface with participating those centers when contact with the air and density of surface oxide atoms in SEM investigations increase to 17-17.5% (Figure 1 and Figure 2).

Formed electrons with \(E_{\delta-e} > 10^3\) eV energy as a result of radiation processes under the influence of neutron flux transmitted from Si particles to contact area and causes ionization, excitation and decay processes in gas (O\(_2\), H\(_2\)O, N\(_2\) etc.) environment [42]. Intermediate products of O, O\(^{-}\), OH, H, OH\(^{-}\), H\(^{+}\) etc. are cause to oxidation of surface atoms. As a results of these processes increasing number of oxidized atoms on surface of nano Si which irradiated by epithermal neutrons (Figure 1). That’s why the amount of oxygen increase from 17.5% to 20.4% on nano Si surface irradiated by epithermal neutrons during \(\tau = 20\) hours.

As result of above mentioned processes, generated electrons and holes in nano Si particles migrate to surface level and formed new charged surface levels. These kind of charged and chemical active states are caused to agglomeration processes. Therefore, the size of irradiated nano Si particles 1.5 - 40 times bigger than primary samples (Figure 1).

The \(\delta\) electrons can be capture by structure defects and impurities as a result of interaction between ambient atoms and electron shells which formed in nano Si environment under the influence of ionization radiation of radiation capture products of \(^{30}\text{Si}\) and impurities which contain the part of ionized nano Si.
Figure 2. EDX spectra and the results of elemental analysis of nano Si before and after irradiation.

\[ p + L_d \rightarrow L(p), \]  
\[ n + L_A \rightarrow L(n), \]  
\[ n + Mn^{+n} \rightarrow Mn^{+(n-1)}, \]  
\[ p + SiO \rightarrow SiO^{-}. \]  

In here, \( L_d \) – structure defect of donor, \( L_A \) – structure defect of acceptor, \( Mn \) - polycharged transition elements, = Si-O – oxidized surface silicon atoms. Most of \( p, n \) and \( L(p), L(n) \) localized states of hole and electrons which formed by process (24) are paramagnetic and can detected by EPR spectroscopy.

Some transition elements in Si environment plays center role and ionized by capturing holes [43, 44]. Some of these elements are paramagnetic in nano Si. In the EPR spectrum of irradiated nano Si samples the lines of paramagnetic transition elements observed in the range of \( B \leq 2000 \text{G} \) Figure 3 (control sample). These center are relaxation fast and the value of \( g \) factor are range of \( g \approx 3.5 \div 5.0 \).
The transition elements convert to other nucleus by neutron capture processes in the neutron irradiated samples and the values of $g \approx 3.5 \div 5.0$ not observed. There are $\equiv \text{Si}^+; \equiv \text{SiO}$ paramagnetic radical states in the irradiated samples and observed lines in range of $g = 2.1 - 2.2$ in EPR spectra (Figure 3 and Figure 4).

$L(n)$ - electron, $L(p)- \equiv \text{SiO}^-$ hole centers formed as a result of (25)-(28) processes by participating non-equilibrium charge carriers in irradiated samples. Usually these centers have relatively deep barriers and are thermally stable. Therefore, in the EPR spectra for after 8 day irradiated by neutrons, observed lines which belonging to both type of centers (Figure 3 and Figure 4). In the range of $g = 1.5 \div 5.0$ there are not observed lines for transition metals, because the spectra
of paramagnetic centers with \( g \approx 2.0 \div 2.4 \) factors measured in the range of \( B = 3300 \div 3350 \) G (Figure 4). Indeed, observation of saturation in the line intensity with \( g \approx 2.002 \) value by increasing of field has prove that its belong to localized electron. This part observed as sharp intensive line in the center of Figure 3. The hole centers which characteristic for silicon containing materials observed as wide spectra for irradiated and non-irradiated samples according to \( g \approx 2.02 \) values. Comparison of intensity of the EPR spectral lines of the irradiated and primary nano Si samples shows that, the density of paramagnetic localized charge centers increase approximately 4 times when irradiated by neutrons during the 20 hours. All of the localized charge carriers don’t generate paramagnetic centers by (25) and (28) processes. Emergence of localized charge carriers in nano Si can be great importance elucidate for explanation of changing of the physical properties in nano size irradiated materials.

Conclusions

The scattering and radiation capture of macroscopic cross-section processes in natural \( ^{28}\text{Si} \), \( ^{29}\text{Si} \), \( ^{30}\text{Si} \) isotopes, the release processes of ionization and brake beams has been monitored in nano Si matrix based on \( \beta \)-rays of formed radioactive Si-31 isotope under the influence of epithermal neutron flux during the 20 hours.

It has been determined that, the energy of \( \beta \)-rays of \( ^{31}\text{Si} \) isotope in Si environment mainly expending to ionization processes and formed free electron, hole and other defect states. An empirical assessment has been carried out for additional charge carriers under the of influence of irradiation as a result of radiation capture processes of the main composition and impurities in environment and the size of investigated nano silicon samples. Surface properties and transition elements has been studied by EPR investigations as a biographical paramagnetic centers and determined features of relaxation processes. Surface active states of non-irradiated nano silicon are caused to oxidation by other components. Charge carriers and structure defects which formed as a result of irradiation increased chemical activation and this caused to oncrease oxidation rate of surface.

As a result of nuclear and radiation processes has been observed localized products of non-equilibrium charge carriers in EPR spectra of irradiated samples under the influence of neutron flux.

References