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Physics

Determination of the Laws and Mechanisms of Degradation of Thermoelectric Properties of Silicon-Germanium Alloys during Irradiation in Reactor

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ABSTRACT. Experimental results of relative growth of specific electric resistance and of thermo-emf coefficient in highly phosphorus- and boron-doped silicon-germanium alloys during their irradiation in a reactor were analyzed and generalized. The mechanism and generalized description of the laws of thermoelectric parameters degradation in reactor-irradiated n- and p-$Si_{0.7}Ge_{0.3}$ alloys are offered. The study is conducted within the bounds of the model of various damaging irradiation doses and changes in the target composition, and thus within the framework of various damage abilities and degradation of the alloy parameters. *© 2009 Bull. Georg. Natl. Acad. Sci.*

***Key words**: silicon, germanium, irradiation, damage dose, properties, degradation.*

Thermoelectric transducers of thermal reactor radiation into electric power have been used in spacecraft-borne nuclear power plants (NPP) since the 1960s. Since then NPPs with thermoelectric generators (TEG) have been successfully used as efficient power sources in various purpose near-Earth and interplanetary satellites and vehicles. Quite a few works are dedicated to the investigation of thermoelectric parameters of highly doped silicon-germanium alloys during their irradiation in nuclear reactors [1-4].

The necessity to proceed with the studies of electric and physical parameters changes in the irradiated silicon-germanium alloys is caused by the growing needs of spacecraft power engineering, and is an urgent problem of radiative study of materials. To present the grounds and provide proper work of NPP with high operation life it is necessary to know the degradation rate of semiconductor and other macroscopic parameters of thermoelectric materials during their irradiation in reactors. Radiative study of materials has not provided comprehensive solution of the problems associated with the prediction of the macroscopic features degradation in the irradiated materials. Neither sufficient experimental data, nor comprehensive theoretical basis is available, which would provide an opportunity to predict degradation of parameters in the irradiated materials. Thus it becomes necessary to conduct long and expensive full-scale TEG testing in reactors in each specific case.

To be able to predict, to provide technical grounds and safe operation of spacecraft NPPs it is expedient to define the laws and mechanisms of degradation of TEG semiconductor material properties.

The present work continues the investigation of the laws and mechanisms of the reactor irradiation effect on thermoelectric parameters of silicon-germanium alloys

[4]. Alloys doped with phosphorus and having natural boron isotope content $N_n \geq 10^{20}$ cm^{-3} were studied in the water-moderated reactor (BBP-M) at the Institute of Nuclear Researches, National Academy of Sciences of Ukraine, using mixed neutron energy spectrum. The alloys were irradiated with fast neutron fluences of up to $\Phi_f = 4\cdot10^{20}$ n.cm^{-2} and flows F_f=2.3·10^{20} n.cm^{-2} and thermal neutron fluences of up to Φ_T = 6.25Ì10^{20} n.cm^{-2} and flows F_T=3.74 ·10^{13} n.cm^{-2}c^{-1} in 773-973 K target temperature range [3].

The threshold value of fast neutron fluences, above which silicon-germanium alloys show sharp growth of specific electric resistance, p, Ohm.cm and of thermo-emf coefficient -α, μV·K^{-1} amounts to $\Phi_f \approx 6\cdot10^{18}$ n.cm^{-2} in the alloys of n-type (electron) conduction, and $\Phi_f \approx 1\cdot10^{18}$ n.cm^{-2} in those of the p-type (hole) one.

In silicon-germanium alloys attainment on saturation of the dose dependences of α and ρ is observed at fluence $\Phi_f \approx 1\cdot10^{20}$ n.cm^{-2} in materials of n-type conduction, and $\Phi_f \approx 2\cdot10^{19}$ n.cm^{-2} for those of the p-type one.

By the end of reactor irradiation specific electric resistance, ρ of the alloys of n-type conduction increased, compared to the initial value, ρ_o, $\rho/\rho_o \approx$20-33 times, while in the alloys of p-type conduction - $\alpha/\alpha_o \approx$6-8 times; thermo-emf coefficients of the alloys of n-type conduction increased $\alpha/\alpha_o \approx$1.8 – 2 fold, while that of the alloys of p-type conduction, $\alpha/\alpha_o \approx$1.4 – 1.7 fold.

Alloys of n-type conduction demonstrate restoration of thermoelectric parameters up to their initial values during programmed thermal annealing in the reactor, while minor improvement is observed in the alloys of p-type conduction.

Experimentally observed laws of shifts of specific electric resistance and thermo-emf coefficient in n-$Si_{0.7}Ge_{0.3}$ towards larger fluences, compared to p-$Si_{0.7}Ge_{0.3}$ [3] are unconditionally connected with the presence of 20 % ^{10}B nuclides in the doping impurities. He and Li atoms, products of ^{10}B nuclide fission possess large kinetic energy and cause additional (compared to n-$Si_{0.7}Ge_{0.3}$ alloy) damage to the matrix. Consequently, irradiation fluences being equal the concentration of defects in the crystalline structure of the material of p-type conduction will be higher than in that of the n-type one.

To characterize radiation damage of the alloys [3] total quantity of irradiating neutrons used per unit target area during *t* time, sec, i.e., radiation fluence made up Φ=F·t, par.cm^{-2}, where F, par.cm^{-2}sec^{-1} is a flow of bombarding neutrons per unit target area per unit time.

To determine the laws and mechanisms of radiation damage, and thus degradation of macroscopic parameters of solid bodies it is necessary to know not only the quantity of bombarding neutrons, i.e., fluence, but also the number of observed displaced atoms (vacancies), i.e. radiation defects.

Physically radiation dose, equal to the total number of displacements (vacancies) per atom of irradiated target, D, dpa is a more valid measure of radiation damage [5]. It shows how many times each atom has been displaced from the lattice site when irradiated by neutron fluences, Φ, par.cm^{-2}. This relative ratio of the displaced atoms (dp)-N_{dp}, cm^{-3} to the target atomic density, N_{SiGe}, cm^{-3}, i.e., N_{dp}, cm^{-3}/N_{SiGe}, cm^{-3}=D, dpa. Then, the ratio D/Φ=d, dpa.par^{-1}cm^{-2} will be the ability of defect formation, rate of defects formation by a separate bombarding particle, while the total quantity of displacements (vacancies) per irradiated target atom can be considered as a quantitative feature of the ability of a bombarding particle to form defects.

Total damaging dose, $\Sigma D = D^{nuc} + D^{elas}$, dpa for p-$Si_{0.7}Ge_{0.3}$ is a total damaging dose of displaced atoms during elastic collisions of helium and lithium atoms, D^{nuc} and fast neutrons, D^{el}, dpa with atoms of the target (He, Li, B, Si, Ge). In the case of n-$Si_{0.7}Ge_{0.3}$ irradiation dose, ÓD, dpa is only total damaging dose of displaced atoms during elastic collisions of fast neutrons with energies of 100 keV, D^{elas}, dpa with the atoms of the target (P, Si, Ge).

The calculations do not take into consideration the distribution of the neutron energy spectrum in the reactor, evolution and radiation defects annealing. The calculation is made for fast neutrons with energies of 100 keV and for thermal neutrons.

During capture of fast neutrons of 100 keV with cross-section σ_f=1.6 barn, and of thermal neutrons, σ_T=3.837 b [6] ^{10}B nuclides are known to fission as follows:

$$^{10}B + n \rightarrow {}^{4}He(1471\ keV) + +7Li(839\ keV) + \gamma(471\ keV)\ 93\ \% \quad (1)$$

$$^{10}B + n \rightarrow {}^{4}He(1777\ keV) + 7Li(1010\ keV)\ 7\ \% \quad (2)$$

Damaging alloy irradiation dose depends on nuclear-physical constants of absorption cross-section and on elastic neutron collisions with the matrix atoms [6,7], as well as on the energy and mass of initially knocked-on atoms (IKA) of the matrix. However, it is independent of the matrix temperature, though the temperature of irradiation and of the following annealing in many respects determines the damageability and changes in the parameters of the irradiated materials.

Calculation of the damaging dose of irradiation was made by a method similar to that described in [8]. Calculation of total IKA energy, released in the cascade of elastic collisions with the target atoms was made using the known method of interpolation of the table data of ions and the target [9]. Irradiation doses were calculated using the modified cascade function [5] and equation

$$D = 0.4 \cdot N \cdot E_{el}/E_d \cdot N_M, \text{ dpa}, \qquad (3)$$

where, N, ika.cm^{-3} and N_M=4.83·10^{22} at/cm^3 are the numbers of IKA and matrix atoms per unit volume, respectively; E_{el}, keV – is the total energy of bombarding particles, released in the cascades of elastic collisions with the target atoms; E_{de}=15eV is the maximum energy of atoms displacement from the target lattice sites. The calculations do not take into consideration recombination, annealing, evolution of the formed vacancies and displaced atoms (the defects are considered as "frozen" ones). In such approximation the calculated values of the ability of defect formation by a single bombarding particle are expressed by the rate of defects formation (displaced atoms and vacancies), while the values of the damaging irradiation dose express only the total value of the formed defects.

Change in the target composition is the next radiation parameter. In the case of p-$Si_{0.7}Ge_{0.3}$ irradiation in reactor changes in the target composition are determined quantitatively by the total number of the products of ^{10}B nuclide fissions during irradiation per target atom, and is expressed by the equations: $D'_1=N_{He}/N_{SiGe}$ and $D'_2=N_{Li+He}/N_{SiGe}$. Then the ability of a single bombarding particle to change the target composition will be expressed by the total number of atoms, formed by this particle per matrix atom, and will be defined by the equations: $D'_1/\Phi = d_1'$, $N_{He}/N_{SiGe}\cdot$He·cm^2, and $D'_2/\Phi = d_2'$, $N_{Li+He}/N_{SiGe}\cdot$He+Li·cm^2, respectively. The work assesses the radiation parameters, and in particular: the

Table

Variation of the relative specific electric resistance of highly doped n- and p-$Si_{0.7}Ge_{0.3}$ alloys during reactor irradiation

D, dpa	D'_1, N_{He}/N_{Li}	D'_2, $N_{He,Li}/N_{SiGe}$	Φ_f, n.cm^{-2}	Φ_t, n.cm^{-2}	ρ/ρ_o	Type
D^{nuc}=0.63 D^{el}=0.12 ΣD=0.75	8.28·10^{-4}	1.66·10^{-3}	4.0·10^{20}	6.5·10^{20}	6-8	p-$Si_{0.7}Ge_{0.3}$
D^{nuc}=0 D^{el}=0.12 ΣD=0.12	- - - -	- - - -	4.0·10^{20}	6.5·10^{20}	20-23	n-$Si_{0.7}Ge_{0.3}$
D^{nuc}=0.63 D^{el}=0.05 ΣD=0.68	8.28·10^{-4}	1.66·10^{-3}	1.72·10^{20}	2.6·10^{20}	6-7	p-$Si_{0.7}Ge_{0.3}$
D^{nuc}=0 D^{el}=6.63·10^{-2} ΣD=6.63·10^{-1}	- - - -	- - - -	1.72·10^{20}	2.6·10^{20}	20	n-$Si_{0.7}Ge_{0.3}$
D^{nuc}=3.66·10^{-3} D^{el}=2.9·10^{-4} ΣD=3.95·10^{-3}	5.16·10^{-6}	1.03·10^{-5}	1.0·10^{18}	1.63·10^{18}	1.1-1.25	p-$Si_{0.7}Ge_{0.3}$
D^{nuc}=0 D^{el}=3.0·10^{-4} ΣD=3.0·10^{-4}	- - - - -	- - - - -	1.0·10^{18}	1.63·10^{18}	1.25	n-$Si_{0.7}Ge_{0.3}$
D^{nuc}=0 D^{el}=1.76·10^{-3} ΣD=1.76·10^{-3}	- - - - -	- - - - -	6.0·10^{18}	9.75·10^{18}	2.7	n-$Si_{0.7}Ge_{0.3}$

ability of separate bombarding particles to generate defects and to change the matrix composition, as well as the defecting irradiation dose and change in the target composition in n- and p-$Si_{0.7}Ge_{0.3}$ alloys.

The table below presents the results of the reactor radiation effect on the specific electric resistance of highly doped silicon-germanium alloys of n- and p-conductance.

The table also presents the calculated values of basic radiation parameters and irradiation conditions. It should be noted that total burn up of ^{10}B nuclides in the matrix occurs during the irradiation by thermal neutron fluences of $\Phi_T=2.6\cdot10^{20}n\cdot cm^{-2}$.

Comparison of the results shows that irradiation of fast neutron fluences being equal, $\Phi_f=4.0\cdot10^{20}$, $1.72\cdot10^{20}$ and $1.0\cdot10^{18}$ $n\cdot cm^{-2}$ irradiation dose for p-$Si_{0.7}Ge_{0.3}$ alloys is substantially higher than that for n-$Si_{0.7}Ge_{0.3}$.

When such or any other thermal neutron irradiation fluences are used, impurity atoms of helium and lithium, products of ^{10}B nuclide fission appear in p-$Si_{0.7}Ge_{0.3}$ in contrast to n-$Si_{0.7}Ge_{0.3}$ alloys, which radically change the composition, and thus defectability of the targets.

The observed pattern of shifts in electric conduction and thermo-emf in n-$Si_{0.7}Ge_{0.3}$ towards larger fluences, $\Phi_f=6.0\cdot10^{18}$ $n.cm^{-2}$, compared to p-$Si_{0.7}Ge_{0.3}$, $\Phi_f=1.0\cdot10^{18}$ $n.cm^{-2}$ is explained by approximately similar values of the matrix damaging irradiation dose, $\Sigma Ddpa=1.76\cdot10^{-3}$ and $\Sigma Ddpa=3.95\cdot10^{-3}$, respectively.

Irradiated materials are known to form highly stable multi-vacancy complexes, which in many respects define their macroscopic parameters and radiation phenomena, that take place. It was found that highly stable helium multi-vacancy complexes had an effect on the physical and mechanical parameters of boron containing materials irradiated in the reactor and by helium ions [11-13].

When p-$Si_{0.7}Ge_{0.3}$ was irradiated in the reactor it was found that due to high mobility of inter-site helium atoms highly stable helium-multi-vacancy complexes are formed in the target. The presence of helium in the irradiated p-$Si_{0.7}Ge_{0.3}$ alloys provides for the formation and accumulation of additional complexes of defects of radiation origin in the crystalline structure. Evolution of helium-multivacancy complexes in the irradiated materials quite satisfactorily explains the experimentally observed patterns of changes in electric conduction and thermo-emf in n-$Si_{0.7}Ge_{0.3}$ and p-$Si_{0.7}Ge_{0.3}$ with the increase of the damaging dose, irradiation temperature and intra-zone annealing. In particular, during the processes of programmed thermal annealing inside the reactor the level of thermoelectric parameters restoration in n-type alloys is substantially higher than that in the p-type alloys.

During the irradiation of n- and p-$Si_{0.7}Ge_{0.3}$ alloys with similar fluences of fast neutrons the damaging dose, and thus radiative defectability and changes in the target compositions are different. Consequently, the effect of the reactor irradiation on the thermoelectric parameters of n- and p-type alloys will also be different, depending on the conditions of irradiation and thermal treatment.

Substantial increase of radiation stability in the p-type alloys is possible with changing ^{10}B nuclides by the ^{11}B ones.

Thus, the developed model of differing damaging irradiation doses and changes in the target composition contains a unified description of the laws, and defines the mechanisms of changes in the electrical and physical parameters in n- $Si_{0.7}Ge_{0.3}$ and p-$Si_{0.7}Ge_{0.3}$ alloys during their irradiation and thermal treatment in the reactor. Earlier criteria and common mechanism of covalent semiconductors amorphisation during ion implantation and irradiation with any particles were defined within the framework of the model [14].

The calculated values of the damaging irradiation dose and changes in the target composition satisfactorily explain the observed patterns and mechanism of changes in thermoelectric parameters of n- and p-$Si_{0.7}Ge_{0.3}$ alloys in the reactor and qualitatively agree with known published data [1-4]. The effect of lithium impurity atoms on the thermoelectric parameters of *p*-type materials has not been defined.

ფიზიკა

რეაქტორში დასხივების დროს სილიციუმ-გერმანიუმის შენადნობების თერმოელექტრული თვისებების დეგრადაციის კანონზომიერებათა და მექანიზმების დადგენა

გ. ბოკუჩავა*, ა. გულდამაშვილი*, გ, დარსაველიძე*, ც. ნებიერიძე*, ა. სიჭინავა*

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განხორციელებულია რეაქტორში დასხივებული n- და p- $Si_{0,7}Ge_{0,3}$ შენადნობის თერმოელექტრული თვისებების ცვლილების კანონზომიერებათა და მექანიზმის ერთიანი აღწერა. იგი ემყარება მბომბავი ნაწილაკების რადიაციული დეფექტების გენერაციისა და სამიზნის შემცველობის განსხვავებულ უნარს, რაც ხვრელურ შენადნობში ჰელიუმისა და ლითიუმის წარმოქნითაა გამოწვეული. სამიზნეების ჩქარი ნეიტრონების ერთიდაიგივე ფლუენსით დაბომბვისას დასხივების დამანგრეველი დოზები და შემადგენლობის ცვლილებები განსხვავებულია. შესაბამისად, განსხვავებულია დასხივების ზეგავლენა შენადნობების თვისებებზე.

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