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Physical Chemistry

Internal Friction Temperature Spectra in Electron-Irradiated SiGe Alloys

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ABSTRACT. SiGe alloys' bulk crystals are characterized by prospects of high application in micro- and optoelectronics as a basic semiconductor material. The problem of producing SiGe alloys bulk monocrystalls of large diameter has not been solved yet due to the specific difficulties of the crystal growth technology. This concerns the SiGe alloys with high Si or Ge content. Based on the above, a complex investigation of dynamic mechanical characteristics of subsystems of structural defects of SiGe alloys under different external impacts (deformation, radiation, thermal cycling) acquires great importance. Internal friction and shear modulus temperature dependence of the monocrystalline SiGe alloys with Ge up to 3 at % content grown by Czochralski technique is studied in initial and electron irradiated states. Dislocation origin relaxation processes and modulus defects are revealed in a temperature interval of 400-800^{0}C in the internal friction temperature spectra of the initial samples. It is shown that after electron irradiation intensity of relaxation internal friction in the vicinity of 280^{0}C increases and activation parameters of high temperature relaxation processes reveal raising by 10-15%. Electron irradiation causes a decrease in the activation energy values of dislocation origin relaxation processes in the temperature range of 400-800^{0}C. It is opined that these changes might be caused by a decrease in the dislocation mobility in the Cottrell atmosphere enriched by the radiation defects. *© 2019 Bull. Georg. Natl. Acad. Sci.*

Key words: internal friction, dislocation, radiation defect, thermal annealing

The investigation of defects in SiGe alloys' bulk crystals was generally carried out by the internal friction method, which is distinguished by high sensitivity to the mechanical stress field formed in the vicinity of crystalline lattice defects. It makes it possible to effectively implement identification of defects of semiconductor SiGe alloys bulk crystals, to establish mechanisms of their influence on the structural sensitive physical-mechanical and electrophysical properties. Such research will help to solve the problem of creating highly efficient semiconductor structures and devices with controllable parameters based on SiGe alloys.

The contribution of a dislocation structure in relaxation and hysteretic processes of torsion oscillations damping in SiGe alloys' bulk crystals has been studied [1-3]. Decrease of the activation characteristics of relaxation processes of dislocation origin is shown by influence of a relatively small content of Ge (1-3 at %). Reduction by ~15% in the microplastic deformation characteristics has been revealed at 600-650ºC temperatures in $Si_{1-x}Ge_x$ (x≤0.02) alloys containing dislocations of 10^4-10^5 cm^{-2} densities [1]. An additional reduction of internal friction activation characteristics has been revealed in $Si_{1-x}Ge_x$(x≤0.01) alloys doped with As or B of 10^{18}-10^{20} cm^3 concentration [4]. SiGe alloys are characterized by different types of dislocations with distinctly different energetic and dynamic parameters [5-7]. This conditions the formation of complex internal friction spectra related to the motion of dislocations.

Relaxation maximum with activation energy ~1.4 eV was revealed at 280°C temperature at ~1 Hz frequency in internal friction spectrum of p-type monocrystalline $Si_{0.98}Ge_{0.02}$ irradiated by high energetic electrons of fluence ~10^{13} cm^{-2}. Its relation to the radiation-induced vacancy-oxygen complexes is supposed [3].

SiGe bulk crystals were grown by the Czochralski method in argon atmosphere. Seeds of Si single crystal with (111) orientation were used for the growth of the SiGe crystals. Microstructure was investigated on the optical microscope NMM-80RF/TRF. Electrophysical characteristics were determined in the constant magnetic field of 0.5 Tesla induction on the Ecopia HMS-3000 device by Hall effect measurements.

Optical absorption spectra in the range of 3-28µm of IR irradiation were studied on Cary 660 FTIR Spectrometer. Investigations of temperature dependent internal friction and shear modulus were carried out on the vacuum device by registration of logarithmic decrement of damping and frequency of free torsion oscillations in the ranges of 20-800ºC temperature and 0.5-5.0 Hz frequency. The measurements were conducted at 2ºC/min heating velocity.

SiGe samples of $[\bar{2}11]$ orientation and 0.8x0.8x(30-35) mm^3 sizes were used for investigating dynamic mechanical properties. Other researches were carried out on the mechanical double-polished 500 µm thickness plates of (111) orientation.

The activation energy of relaxation internal friction maxima was determined by the formula [8]:

$$H = R\cdot\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\ln\frac{f_2}{f_1}, \qquad (1)$$

where R is gas constant, T_1, T_2 are temperatures of maxima at f_1 and f_2 frequencies.

The values of frequency factor $\frac{1}{\tau_0}$ were determined from the known equation $\omega_{\max}\cdot\tau = 1$, where $\omega_{\max} = 2\pi\cdot f_{\max}$ and $\tau = \tau_0\cdot\exp\left(\frac{H}{RT_{\max}}\right)$.

Microstructure of Si, $Si_{0.995}Ge_{0.005}$, $Si_{0.988}Ge_{0.012}$ and $Si_{0.97}Ge_{0.03}$ alloys on the (111) planes is characterized by a non-uniform distribution of dislocation etch pits. The dislocation density is increased in Ge-doped crystals. Dislocation groups are often fixed in the microstructure of $Si_{0,97}Ge_{0,03}$

Table 1. Electrophysical characteristics of monocrystalline Si and SiGe alloys

Experimental Samples	Dislocation density, cm^{-2}	Current carriers concentration, cm^{-3}			Current carriers mobility, $cm^2v^{-1}\cdot s^{-1}$		
		Initial	Electron-irradiated	Annealed at 300ºC , 1 h.	Initial	Electron-irradiated	Annealed at 300ºC , 1 h.
Si	$2\cdot10^4$	$7\cdot10^{13}$	$1\cdot10^{14}$	$6\cdot10^{13}$	430	400	440
$Si_{0.995}Ge_{0.005}$	$5\cdot10^4$	$8\cdot10^{13}$	$2\cdot10^{14}$	$7\cdot10^{13}$	410	370	420
$Si_{0.988}Ge_{0.012}$	$7\cdot10^4$	$5\cdot10^{13}$	$5\cdot10^{13}$	$2\cdot10^{13}$	425	380	435
$Si_{0.97}Ge_{0.03}$	$1\cdot10^5$	$5\cdot10^{13}$	$8\cdot10^{13}$	$4\cdot10^{13}$	450	390	460

alloys. The changes of density and distribution of dislocations in the microstructure of the electron-irradiated samples have not been practically revealed. Table 1 shows the dislocation densities revealed in the investigated samples.

All samples in the initial state are characterized by p-type conductivity, low concentration and mobility of current carriers.

Thermal annealing at temperatures of 300-400ºC in vacuum does not affect the electrophysical characteristics of non-irradiated Si, $Si_{0.995}Ge_{0.05}$ and $Si_{0.988}Ge_{0.012}$ samples. $Si_{0.97}Ge_{0.03}$ sample in annealed state is characterized by a weak increase of hole mobility. This is conditioned by annihilation of electrically active technological defects distributed in stress fields near the Ge atoms and in the impurity atmosphere around dislocations.

In electron-irradiated samples a significant increase in current carriers' concentration and their mobility reduction are revealed. Such changes are conditioned by the point defects and their simple complexes formed by irradiation. Thermal annealing of all the samples irradiated with high-energy electrons at 300°C for 1h causes a reduction in the concentration of holes and an increase in the mobility to the initial level. Obviously, the annealing causes transformations in the structure of radiation defects and a reduction in the concentrations of electrically active defects.

Fig. 1 shows IR absorption spectra of the (111) surfaces of Si plates (thickness ~500 μm) in the initial and electron-irradiated states. In both spectra, overlapping maxima are revealed in a wave number range of 500-1500 cm^{-1}. Maxima of vacancy-oxygen (VO) and fundamental oscillations of crystalline lattice exist near points of 605 and 1105cm^{-1}. The weak absorption band 885-888cm^{-1} relates to the neutral charge states of the (VO) defects [9]. In the electron-irradiated Si a new band 2340-2361 cm^{-1} appears. Apart from the above, several traces of the bands of complex composition are revealed in the high frequency area. They may be stipulated by divacancies of different electrical charge states. Thermal annealing at 600ºC temperature reduces to a zero the intensity of high-frequency bands in the range of 3000-5500cm^{-1}.

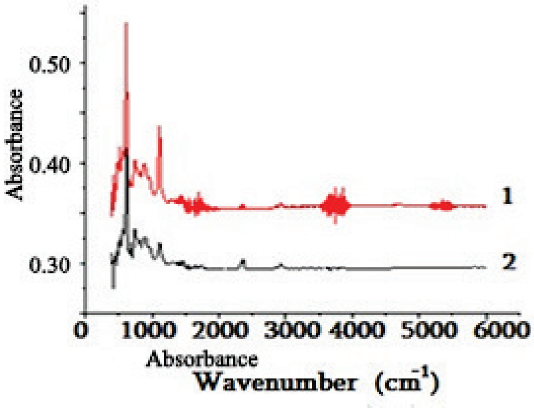

Fig. 1. IR absorption spectra of monocrystalline Si. 1 – initial state; 2 – after electron irradiation.

The optical absorption spectrum of $Si_{0.995}Ge_{0.005}$ alloy in the initial state is practically identical to the initial spectrum of Si. A weak reduction in the wave number and intensity of clearly expressed maxima is noticeable. In the electron-irradiated state, the traces of absorption bands are more clearly revealed in the high frequency area. The intensity of maxima related to the C and O impurities revealed near 605 and 1106 cm^{-1} respectively decreases. Their decrease is more clearly revealed in $Si_{0.97}$ $Ge_{0.03}$ alloy absorption spectrum (Fig. 2). The absorption band of complex composition and intensity is additionally formed in 1200-1400 cm^{-1} interval. The intensity of maxima related to the 885 cm^{-1} band is slightly changed.

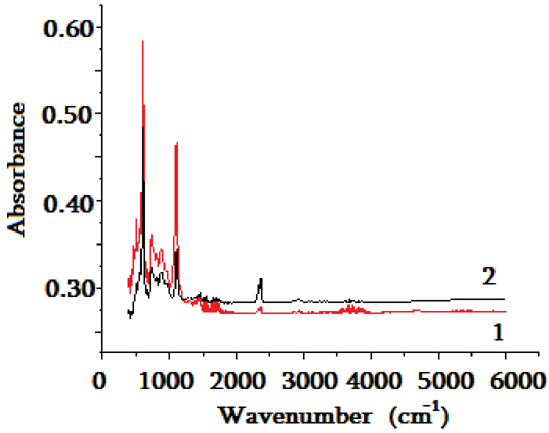

Fig. 2. IR absorption spectra of monocrystalline $Si_{0.97}Ge_{0.03}$ alloy. 1 – initial state; 2 – after electron irradiation.

The IF temperature spectrum $Q^{-1}(T)$ of monocrystalline Si of (111) orientation is characterized by wide maxima in the 100-800°C temperature range (Fig. 3).

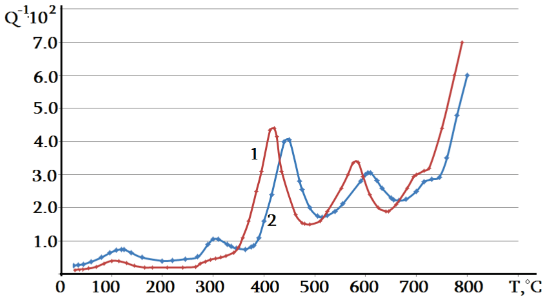

Fig. 3. Temperature dependence of internal friction of monocrsyatlline Si of (111) orientation. 1. Initial state, f_0=1.2Hz; 2. after electron irradiation, f_0=1.1Hz.

Shapes of the IF maxima are distorted by their overlapping and exponentially growing background. The Intensity of the IF background and maxima in 400-800°C temperature range significantly increase at high strain amplitudes of 10^{-4}-10^{-3}. This circumstance reveals their dislocation nature.

All IF maxima change their critical temperature by changing oscillations frequency. According to the well-known theory [8], they are of relaxation origin. This is also confirmed by revealing the shear modulus defects being proportional to the maxima intensity (Fig. 4).

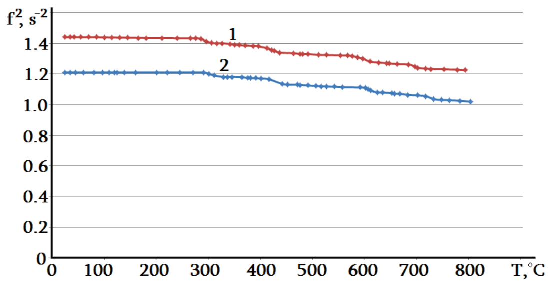

Fig. 4. Temperature dependence of shear modulus of monocrystalline Si of (111) orientation. 1. Initial state, f_0=1.2Hz; 2. After electron irradiation, f_0=1.1Hz.

Table 2. Activation characteristics of internal friction relaxation maxima.

Samples	Temperature of IF maxima, °C		Activation energy, eV		Frequency factor, s^{-1}	
	Initial state	After electron irradiation	Initial state	After electron irradiation	Initial state	After electron irradiation
Si	-	100	-	0.90	-	$6.5 \cdot 10^{12}$
	280	300	1.35	1.40	$1 \cdot 10^{13}$	$2 \cdot 10^{13}$
	410	420	1.50	1.60	$6 \cdot 10^{11}$	$2 \cdot 10^{12}$
	600	615	1.65	1.80	$2 \cdot 10^{10}$	$6 \cdot 10^{10}$
	710	725	2.10	2.20	$3.5 \cdot 10^{11}$	$6.3 \cdot 10^{11}$
$Si_{0.995}Ge_{0.005}$	100	100	-	0.90	-	$6 \cdot 10^{12}$
	280	300	1.30	1.50	$3.5.10^{12}$	$6.3 \cdot 10^{13}$
	400	415	1.60	1.75	$4.4 \cdot 10^{12}$	$3.4 \cdot 10^{13}$
	590	600	1.70	1.80	$6 \cdot 10^{10}$	$2 \cdot 10^{11}$
	700	720	2.00	2.10	$1.5 \cdot 10^{11}$	$2 \cdot 10^{11}$
$Si_{0.988}Ge_{0.012}$	100	100	0.9	0.9	$5 \cdot 10^{12}$	$5 \cdot 10^{12}$
	285	285	1.3	1.3	$4 \cdot 10^{12}$	$8 \cdot 10^{12}$
	400	405	1.6	1.65	$6 \cdot 10^{12}$	$7.5 \cdot 10^{12}$
	590	600	1.7	1.75	$8 \cdot 10^{11}$	$1 \cdot 10^{12}$
	690	700	1.8	1.85	$6 \cdot 10^{11}$	$8.5 \cdot 10^{11}$
$Si_{0.97}Ge_{0.03}$	100	100	0.90	0.90	$1 \cdot 10^{13}$	$1 \cdot 10^{13}$
	280	290	1.30	1.45	$3.5.10^{13}$	$5 \cdot 10^{13}$
	390	400	1.65	1.70	$2 \cdot 10^{13}$	$2.2 \cdot 10^{13}$
	600	605	1.65	1.75	$3 \cdot 10^{10}$	$7 \cdot 10^{10}$
	685	700	1.90	2.00	$6 \cdot 10^{10}$	$1.7 \cdot 10^{11}$

The values of activation energy and frequency factors are presented in Table 2 [7].

Irradiation of monocrystalline Si by high energy electrons stipulates an increase in the IF intensity at 100 and 280ºC and a weak rise in the critical temperatures of relaxation maxima in the 400-800ºC temperature range. Electron irradiation of monocrystalline Si causes a rise in the activation characteristics of high-temperature relaxation processes in comparison with identical values of Si in the initial state. Thermal annealing at 600ºC for 3 h of electron-irradiated samples of Si completely suppresses the IF maxima at 100 and 280ºC temperatures. In the annealed state the IF exponential background shifts towards high temperatures.

The following peculiarities have been revealed in the IF temperature spectra of the monocrystalline SiGe alloys irradiated by high energy electrons (Fig. 5). An increase in the content of Ge stipulates a reduction in the intensity of IF maxima at 100 and 280ºC temperatures; however, their activation characteristics remain unchanged in comparison with the identical values in nonirradiated states. The IF maxima revealed in the 400-800ºC range are shifting by 15-20ºC towards high temperatures. Respectively, an increase in the activation characteristics is clearly shown (Table 2).

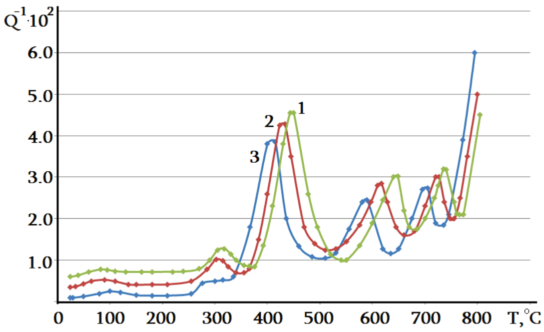

Fig. 5.Temperature dependence of internal friction of monocrsyatlline SiGe alloys after electron irradiation. 1. $Si_{0.995}Ge_{0.005}$, f_0=1.8 Hz; 2. $Si_{0.988}Ge_{0.012}$, f_0=2.0 Hz; 3. $Si_{0.97}Ge_{0.03}$, f_0=2.15 Hz.

Fig. 6 shows temperature changes of shear modulus of electron-irradiated SiGe alloys. At the critical temperatures, the shear modulus defect is revealed in proportion to the relaxation process intensity. Annealing at 600ºC for 3 h in vacuum of SiGe samples causes a sharp reduction in the intensity of the IF maxima at 100 and 280ºC and a slight decrease in the other maxima intensity. A weak reduction of the shear modulus is revealed at critical temperatures.

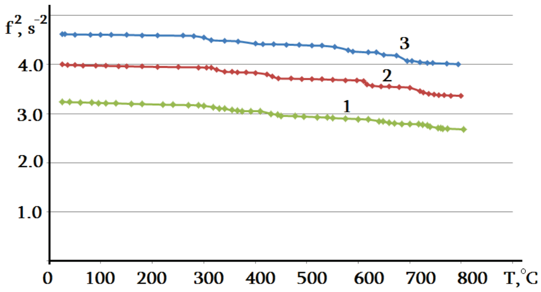

Fig. 6. Temperature dependence of shear modulus of monocrsyatlline SiGe alloys, after electron irradiation. 1. $Si_{0.995}Ge_{0.005}$, f_0=1.8 Hz; 2. $Si_{0.988}Ge_{0.012}$, f_0=2.0 Hz; 3. $Si_{0.97}Ge_{0.03}$, f_0=2.15 Hz.

High-temperature cyclic deformation of SiGe samples at 600ºC stipulates a noticeable increase in the relaxation maxima intensity in the 400-800ºC range and a reduction in their critical temperatures. Consequently, the shear modulus defects increase at the critical temperatures. It should be noted that activation characteristics of the relaxation maxima at 100 and 280ºC temperatures are independent from high-temperature cyclic deformation. Thermal annealing at ≈600ºC for 3 h after high-temperature cyclic deformation causes complete suppression of maximum near 100ºC and a sharp reduction in the relaxation process intensity in the vicinity of 280ºC.

The values of activation energy of 60º-edge dislocations motion in SiGe alloys with different content of Ge and Si are determined by studies of mechanical properties [5,7]. Based on the results of both works, it may be supposed that the IF maxima revealed near 400 and 600ºC temperatures in the investigated samples are stipulated by moving of single kinks on 60°-edge and screw dislocations respectively. It may be supposed, that relaxation maximum in the vicinity of 700°C temperature is connected with generation and migration of double-kinks on the 60°- edge dislocations.

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ფიზიკური ქიმია

შინაგანი ხახუნის ტემპერატურული დამოკიდებულება ელექტრონებით დასხივებულ SiGe შენადნობებში

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SiGe შენადნობების მოცულობითი კრისტალები ხასიათდება მიკრო- და ოპტოელექტრონიკაში საბაზო ნახევარგამტარულ მასალად გამოყენების მაღალი პერსპექტივებით. ტექნოლოგიის სპეციფიკური სირთულეების გამო დღემდე პრაქტიკულად გადაწყვეტილი არ არის SiGe შენადნობების დიდი დიამეტრის მოცულობითი მონოკრისტალების მიღების პრობლემა. ეს ეხება როგორც სილიციუმის, ასევე გერმანიუმის საფუძველზე შექმნილ SiGe შენადნობებს. აღნიშნულიდან გამომდინარე, დიდი მნიშვნელობა ენიჭება სხვადასხვა ზემოქმედებით (დეფორმაცია, რადიაცია, თერმული ციკლირება) SiGe შენადნობების სტრუქტურული დეფექტების ქვესისტემის კრისტალოგრაფიული და დინამიkური მექანიკური მახასიათებლების კომპლექსურ კვლევას. წინამდებარე ნაშრომში შესწავლილია ჩოხრალკის მეთოდით მიღებული საწყისი და ელექტრონებით დასხივებული მონოკრისტალური SiGe შენადნობების (გერმანიუმის კონცენტრაცია 3ატ%-მდე) შინაგანი ხახუნისა და ძვრის დინამიkური მოდულის ტემპერატურული დამოკიდებულება. საწყის მდგომარეობაში შინაგანი ხახუნის ტემპერატურული სპექტრის 400-800°C ინტერვალში გამოვლენილია დისლოკაციური წარმოშობის რელაქსაციური პროცესები და მოდულის დეფექტი.ნაჩვენებია, რომ ელექტრონებით დასხივების შემდეგ რელაქსაციური შინაგანი ხახუნის ინტენსივობა 280°C-ზე იზრდება. ელექტრონებით დასხივება იწვევს 400-800°C ტემპერატურულ ინტერვალში დისლოკაციური წარმოშობის რელაქსაციური პროცესების აქტივაციის ენერგიის სიდიდეების შემცირებას. ასეთი ცვლილებები გამოწვეულია დისლოკაციების ძვრადობის შემცირებით რადიაციული დეფექტებით გამდიდრებული კოტრელის ატმოსფეროში.

REFERENCES

1. Kurashvili I., Bokuchava G., Mkheidze T., Baratashvili I. (2007) Inelastic properties of monocrystaline SiGe alloys. *Bull. Georg. Acad. Sci.,* **175**(4): 62-65.
2. Kurashvili I., Darsavelidze G., Bokuchava G. (2017) *Physica Status Solidi* A, **214** (7): 17001071-17001074.
3. Kurashvili I., Darsavelidze G., Bokuchava G., Chubinidze G., Tabatadze I., Archuadze G. (2018) *Bull. Georg. Acad. Sci.,* **12**(3): 57-61.
4. Kurashvili I., Darsavelidze G. (2015) Mechanical relaxation processes in monocrystalline Si-Ge alloys. Proceedings of the International Conference – Advanced materials and Technology. Tbilisi.
5. Yonenaga I., Sumino K. (1997) Mechanical strength and dislocation velocities in gesi alloys. Journal of Physics, III (7): 2367-2374, France.
6. Yonenaga I., Werner M., Bartsch M., Messerschmidt U., Weber E.R. (1999) Recombination-enhanced dislocation motion in SiGe and Ge, *Physica Status Solidi* **171** (a): 35-40.
7. Yonenaga I. (2013**)** Dislocation dynamics in SiGe alloys. Journal of Physics: Conference Series, (471): 0120021-0120029. doi:10.1088/1742-6596/471/1/012002.
8. Blanter M.S., Golovin I., Neuhauser H., Sining H. (2007) Internal friction in metallic materials. A handbook series: Springer Series in *Materials Science,* 90:539.
9. Londos C.A., Sgourou E.N., Hall D., Chroneos A. J. (2014) Materials science. *Materials in Electronics,* **25**(6) 2395-2410.

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