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Influence of Boron Doping and Thermal Treatment on Internal Friction of Monocrystalline $Si_{1-x}Ge_x(x\leq0,02)$ Alloys

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***Abstract*—**The impact of boron doping on the internal friction (IF) and shear modulus temperature spectra of $Si_{1-x}Ge_x(x\leq0,02)$ monocrsytals has been investigated by reverse torsional pendulum oscillations characteristics testing. At room temperatures, microhardness and indentation modulus of the same specimens have been measured by dynamic ultra microhardness tester. It is shown that boron doping causes two kinds effect: At low boron concentration ($\sim10^{15}$ cm^{-3}) significant strengthening is revealed, while at the high boron concentration ($\sim10^{19}$ cm^{-3}) strengthening effect and activation characteristics of relaxation origin IF processes are reduced.

***Keywords*—**Dislocation, internal friction, microhardness, relaxation.

I. Introduction

CZOCHRALSKI-grown silicon remains the basic material for solid-state electronics. Being the most active impurity in defect-impurity interaction, oxygen forms a variety of defects [1]-[3] that can affect the electrical and optical properties of Si. Furthermore, it should be noted, that p-type boron-doped Czochralski (CZ) silicon solar cells are suffering a light-induced degradation in efficiency up to 2% absolutely, due to specific defects formation. These specific defects are related to the simultaneous presence of boron and oxygen in silicon. For practical photovoltaic application, the most interesting is to find an effective way to suppress the B-O defects in CZ silicon.

Considerable attention has been focused recently on the silicon doped with isovalent impurities (Ge, C, Sn). This is due to the facts that they are electrically inactive and have almost no effect on the initial properties of silicon, but at the same time, being the sources of internal stress, they may have a pronounced effect on defect- impurity interaction [4]-[8]. It is suggested that the germanium addition to CZ silicon crystals would immobilize dislocations when the concentrations of germanium atoms exceeded the oxygen concentration by two to three orders of magnitude [9].

The improved strength of CZ silicon crystals heavily alloyed with germanium is most probably caused due to dislocation immobilization by oxygen atoms located next to germanium atoms [10].

Microhardness of Si-Ge ingots and epitaxial structures were investigated in a wide range of compositions at the room temperature [11], [12]. In both cases, monotonous dependence of microhardness on the composition was observed. Non-monotonous dependence of microhardness on the composition were revealed in $Si_{1-x}Ge_x$ ($x\leq0,15$) solid solutions at 570 °C temperature. The most probable cause of the observed effect is supposed hardening of solid solutions, stipulated by spinodal decomposition and formation of clusters and dispersed precipitates.

Temperature dependent IF and shear modulus of monocrystalline Si-Ge specimens have been investigated [13], [14]. It was established that CZ silicon doping with Ge caused decrease of the activation characteristics of the dislocation origin IF relaxation processes. Increase of Ge concentration in Si-structure also causes a decrease of critical strain amplitudes.

II. Experiment

Present work deals with the investigations of microstructure, electrophysical characteristics, IF and shear modulus temperature dependence and microhardness of boron-doped monocrystalline $Si_{1-x}Ge_x$ ($x\leq0,02$) alloys, obtained by Czochralski method.

Microstructure was investigated by 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 the Hall effect measurements.

IF and squared frequency (f^2), were investigated by the laboratory equipment with reverse torsion pendulum. Measurements of IF and f^2 temperature dependences were carried out in vacuum 10^{-4} Torr. Investigations were conducted in temperature interval of 20-800 °C with heating velocity 2 °C/min in a range of oscillations frequency 0.5-5.0 Hz and strain amplitude $1\cdot10^{-5}$-$5\cdot10^{-3}$.

Studying of microhardness was carried out on Shimadzu dynamic ultra-micro hardness tester DUH-211S. The mechanical parameters (static and dynamic micro hardness, indentation modulus) were studied on the (111) planes of boron-doped Si+2at%Ge substrates by Vickers indenter in loading-unloading test mode. Load range was 3-1500mN, holding time at maximum load was 10s and 5s at unload.

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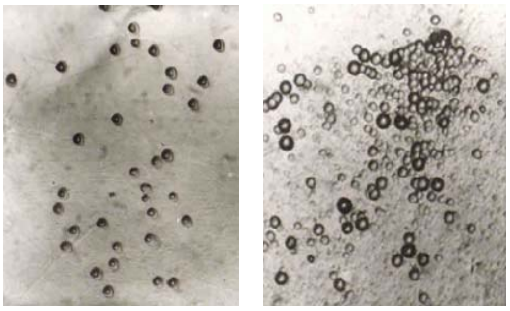
III. Results and Discussion

In microstructure of boron-doped Si-Ge monocrystals by metallographic research on the optical microscope following peculiarities were revealed:

On the (111) plane of Si+1at%Ge:B ($5\cdot10^{15}$ cm^{-3}) and Si+2at%Ge:B ($1\cdot10^{16}$ cm^{-3}) monocrystals dislocation distribution is homogeneous and density varies in $5\cdot10^{3}$-$1\cdot10^{4}cm^{-2}$ interval (Fig. 1 (a)).

Increase of boron concentration up to ~10^{19} cm^{-3} causes inhomogeneous distribution of dislocations and increase of their density up to $5\cdot10^{4}$ cm^{-2}. In some cases, well developed cellular dislocation structure was revealed.

On Fig. 1 are presented microphotographs of etch piths distribution in some monocrystalline Si-Ge alloys.



(a) (b)

Fig. 1 Microstructure of Si-Ge monocrystals (a) Si+2at%Ge:B ($1\cdot10^{15}$ cm^{-3}), (b) Si+2at%Ge:B ($2\cdot10^{19}$ cm^{-3})

Specific real structural state is reflected on electrophysical characteristics of investigated Si-Ge samples as in Table I.

TABLE I
Electrophysical Characteristics of Boron-Doped Si-Ge Monocrystals

Experimental samples	Dislocation density, cm^{-2}	Carriers concentration, cm^{-3}	Carriers mobility $cm^2 \cdot V^{-1} \cdot sec^{-1}$
Si+1at%Ge:B	$5\cdot10^{3}$	$5\cdot10^{15}$	350
Si+1at%Ge:B	$8\cdot10^{3}$	$1\cdot10^{19}$	70
Si+2at%Ge	$1\cdot10^{4}$	$3\cdot10^{14}$	380
Si+2at%Ge:B	$2\cdot10^{4}$	$1\cdot10^{16}$	320
Si+2at%Ge:B	$5\cdot10^{4}$	$2\cdot10^{19}$	60

Table I shows that current carriers mobility of all boron-doped samples are relatively low. Simultaneous presence of Ge and B atoms, as well high density of dislocations apparently cause observed low carriers mobility of investigated Si-Ge specimens.

IF and shear modulus temperature dependences of nondoped and boron-doped Si+1at%Ge and Si+2at%Ge monocrystalline samples were investigated. In IF temperature spectra plurality of maxima and shear defects were revealed. Comparative analysis shows that Si+1at%Ge:B alloy with low boron concentration is characterized by relatively high shear modulus and activation characteristics of relaxation origin IF maxima. Increase of boron concentration leads to reduction of these mechanical parameters. Thermal annealing in vacuum near 800°C reveals decreasing tendency of activation characteristics of IF maxima.

Temperature spectra of IF and shear modulus of nondoped and boron-doped Si+2at%Ge monocrystals were also studied. It is supposed, that IF spectrum of undoped monocrystalline Si+2at%Ge alloys is characterized with intensive maxima at 110, 320, 430, 535,650 and 750 °C temperatures. The first two maxima are imposed on the low intensity background. In the temperature range 400-800 ^{0}C IF background significantly increases. In consequence of presence high intensity background, shape of IF maxima are distorted. Temperature of maxima change, with changing of oscillation frequency from 1.0 to 5.0 Hz. It testifies to the relaxation origin of the pointed IF maxima.

The values of activation energy and frequency factors of IF relaxation processes are presented in Table II.

Weak doping by boron ($5\cdot10^{15}$ cm^{-3}) of monocrystalline Si+2at%Ge practically does not influence on characteristics of IF maxima in 20-400 °C temperature interval. Weak boron doping significantly increases temperature and activation energy of relaxation processes above 400 °C temperature.

Increase of B concentration up to $2\cdot10^{19}$ cm^{-3}, on the contrary, noticeably decreases temperature of IF maxima, causes increase of their intensity. Herewith, it causes reduction of activation characteristics of relaxation processes, observed in 400-800 °C temperature interval (Fig. 2). Shape and temperature of IF maxima, observed below 400°C does not change practically. In this temperature area IF does not depends on strain amplitude. Other IF relaxation maxima have amplitude–dependent character, that shows their dislocation origin [15].

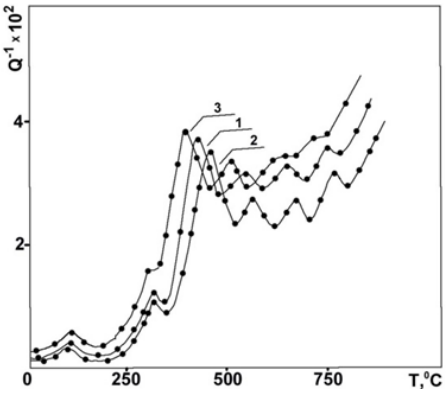


Fig. 2 Temperature dependence of IF of monocrystalline Si-Ge alloys. 1-Si+2at%Ge; 2. -Si+2at%Ge ($1\cdot10^{16}$ cm^{-3}); 3.-Si+2at%Ge:B ($2\cdot10^{19}$ cm^{-3})

After cyclic deformation at the 600 °C is observed increasing intensity of amplitude-dependent IF maxima and decreasing their activation characteristics.

Subsequent annealing at 600°C temperature during 5 hr. decreases of intensity of all IF maxima, increases the values of activation energy and frequency factor of pointed relaxation processes.

Characteristics of relaxation IF maxima at 110 and 320 °C

temperatures do not depend on strain amplitude. They practically do not change under influence of high temperature cyclic deformation and subsequent annealing. It is supposed, that relaxation IF maxima at the 80-120 °C and 280-320 °C temperatures are connected with migration of divacancies and vacancy-oxygen complexes under periodic mechanical stresses.

Absolute values of shear modulus of investigated Si-Ge samples were calculated. Results are presented in Table II. The tendency to hardening at low B concentration and softening at high B concentration are shown in Table II.

Taking into account known activation characteristics of generation of edge- and screw dislocations in silicon, based on [16], it is supposed that in Si-Ge alloy IF maxima relaxation at 430 and 535 °C temperatures are stipulated by motion of individual kinks on 60°- and screw dislocations. Relatively high activation energy (2.1 and 2.35 eV) of relaxation IF processes at 650 and 720 °C, gives possibilities to assume, that these IF maxima are connected with generation and motion of double kinks on screw – and 60°-edge dislocations.

At low concentration of boron ($1\cdot10^{15}$ cm^{-3}) with small atomic radius, dislocation motion in crystalline lattice with local areas of compression becomes difficult. At high concentration of boron (10^{19} cm^{-3}) forces of electric origin dominate. They delocalize electrical bonds near dislocation cores and its motion facilitates. These changes are the reasons of blocking and un-blocking of dislocations in crystalline lattice of Si-Ge:B alloys.

TABLE II
PHYSICAL-MECHANICAL CHARACTERISTICS OF MONOCRYSTALLINE SI-GE ALLOYS

Experimental samples	Shear modulus kg/mm^2	Temperature of IF maxima, °C	Activation energy, eV	Frequency factor, sec^{-1}
p-Si+2at%Ge ($3\cdot10^{14}cm^{-3}$)	4700	110	0.85	$5\cdot10^{12}$
		320	1.35	$6\cdot10^{12}$
		430	1.65	$7\cdot10^{12}$
		535	1.80	$2\cdot10^{12}$
		650	2.05	$8\cdot10^{11}$
		720	2.20	$5\cdot10^{11}$
p-Si+2at%Ge:B ($1\cdot10^{16}cm^{-3}$)	4930	115	0.90	$5\cdot10^{12}$
		320	1.40	$5\cdot10^{12}$
		445	1.75	$7.5\cdot10^{12}$
		550	1.85	$1\cdot10^{12}$
		665	2.15	$3\cdot10^{11}$
		740	2.35	$1\cdot10^{11}$
p-Si+2at%Ge:B ($2\cdot10^{19}cm^{-3}$)	4530	110	0.85	$5\cdot10^{12}$
		315	1.30	$5\cdot10^{12}$
		420	1.60	$4\cdot10^{12}$
		515	1.70	$8\cdot10^{11}$
		635	1.95	$6\cdot10^{11}$
		700	2.10	$4\cdot10^{11}$

Fig. 3 represents dependence of dynamic (DHV) and static/ relaxed (HV) microhardness on penetration depth.

A weakly expressed reverse indentation size effect is observed. As known, such behavior characterizes brittle materials [17]. Also, it is shown a little decreasing of micro hardness with increasing of boron concentration. However, this dependence for static (HV) microhardness is hardly noticeable. Dependence of indentation modulus on penetration depth is shown on Fig. 4.

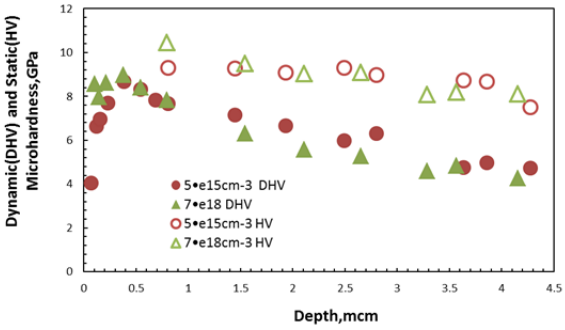


Fig. 3 Microhardness versus penetration depth of boron doped Si-Ge substrates

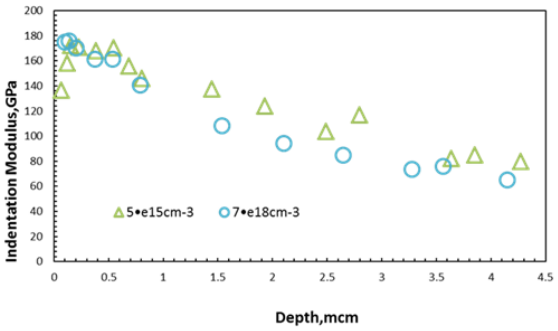


Fig. 4 Indentation modulus versus penetration depth of boron doped Si-Ge substrates

Fig. 4 shows that Si-Ge substrates doped with low boron concentration have relatively high indentation modulus. Increase of boron content up to $7\cdot10^{18}$ cm^{-3} leads to decrease some mechanical parameters. Comparison shows, that behavior of indentation modulus in a wide range of penetration depth is similar to microhardness changes.

It is supposed that low concentration boron atoms forms braking atmospheres around dislocations and decreases their mobility, that stipulates increasing mechanical characteristics. In case of high boron concentration dislocation braking electrical forces weaken, that may be a reason of decreasing mechanical characteristics.

IV. CONCLUSION

In boron doped $Si_{1-x}Ge_x$($x\leq0,02$) monocrsytals in a wide range of temperature relaxation origin IF maxima and nonmonotonous changes of shear modulus have been revealed. It is established, that at low boron concentration (~1015 cm^{-3}) absolute values of shear modulus and activation characteristics of dislocation origin relaxation processes significantly increases. In case of high boron concentration, decrease of shear modulus and activation characteristics of relaxation processes takes place. Pointed changes of activation characteristics are correlated with variations of microhardness and indentation modulus. Obtained results are analyzed in aspect of possible changes of dislocation-boron atoms interaction.

Microscopic mechanisms of dynamic mechanical characteristics changing in bulk Si-Ge monocrystalline alloys is subject of our further investigations.

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