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Dynamical Mechanical Properties of Boron-Doped Monocrystalline Germanium

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ABSTRACT. Microstructure, electrophysical properties and characteristics of dynamical shear modulus and microplastic deformation of boron-doped monocrystalline germanium were investigated. Bulk crystals of germanium were obtained by Czochralski method in [111] crystallographic direction. Boron concentration in monocrystals was changed in the $5\cdot10^{16}$-$5\cdot10^{19}$ cm^{-3} interval. Dislocation density determined by estimation of the quantity of etching pits was changed from 10^3 to $5\cdot10^4$ cm^{-2}. It has been established that an increase of boron concentration in monocrystalline germanium causes a decrease of current carriers mobility and an increase of the absolute value of shear modulus in comparison with undoped specimens. After high temperature annealing tendency to increasing of current carrier mobility, dynamical shear modulus and elastic limit was revealed.

By investigations of internal friction and dynamical shear modulus amplitude dependences of boron-doped monocrystalline germanium the following results were received. The values of elastic limit, dynamical shear modulus and critical strain amplitude of Ge:B monocrystals were determined. It has been established that weakly boron-doped monocrystalline germanium is characterized by high elastic limit, critical strain amplitude and shear modulus. This is due to structure strengthening, caused by an increase of dislocation blocking by boron atoms. In the case of high concentration of boron simultaneously with the strengthening process, "softening" process has taken place. It is determined by fulfillment of broken electron bonds near to dislocation cores that has caused decrease of activation energy of dislocation motion. On the basis of changes of interaction nature of dislocations and boron atoms mechanisms of strengthening and softening processes of structure under the influence of boron were analyzed. *©2012 Bull. Georg. Natl. Acad. Sci.*

Key words: *germanium, internal friction, dynamical shear modulus.*

The working resource and stability of characteristics of devices based on monocrystalline germanium alloys have been determined by dislocations existing in the structure. Despite this, the crystallographic and energetic characteristics of defects, characterizing monocrystalline Ge alloys, their influence on structural-sensitive semiconducting and physical-mechanical properties have not been complexly studied.

Table. Characteristics of structure and properties of Ge:B monocrystals

Specimens	Current carriers concentration, cm^{-3} [111]	Current carriers mobility, $cm^2 \cdot v^{-1} sec^{-1}$, [111]	Shear modulus, kg/mm^2		Relative strain amplitude		Elasticity limit, kg/mm^2	
			[111]	[100]	[111]	[100]	[111]	[100]
Ge	$5 \cdot 10^{15}$	1850	3800	3600	$4 \cdot 10^{-5}$	$7 \cdot 10^{-4}$	0.15	2.66
Ge:B	$1 \cdot 10^{16}$	1600	4150	3950	$1 \cdot 10^{-4}$	$3.5 \cdot 10^{-5}$	0.41	14.5
	$5 \cdot 10^{17}$	1250	4100	3850	$8 \cdot 10^{-5}$	$2 \cdot 10^{-3}$	0.33	8.2
	$8 \cdot 10^{19}$	950	3900	3700	$7 \cdot 10^{-5}$	$1 \cdot 10^{-3}$	0.27	3.9

Investigation results of characteristics of microstructure, electrophysical properties, dynamical shear modulus and microplastic deformation of boron-doped germanium are presented in the present paper.

Bulk crystals of germanium were obtained by Czochralski method in [111] crystallographic direction. Boron concentration in monocrystals was changed in the $5 \cdot 10^{16}$-$5 \cdot 10^{19} cm^{-3}$ range. Dislocation density on the (111) planes was determined by estimation of the quantity of etching pits. Electrophysical characteristics were determined by Hall effect in constant magnetic field.

Amplitude dependence of dynamical shear modulus was investigated by the method of torsion oscillations frequency registration. The absolute value of shear modulus was calculated by comparing the standard and test specimens[1]:

$$G = G_0 f^2 / f_0^2 ,$$

where G_0, f_0 are the values of shear modulus and oscillation frequency of the standard specimen (vanadium) , G, f - the values of shear modulus and oscillation frequency of test crystals. The values of elastic limit were calculated from the equation: $s = G \cdot \varepsilon_{cr}$, where G is a value of shear modulus, $\varepsilon_{cr.}$ - critical strain amplitude, at which distinct revealing of inelastic properties begins.

Ge:B monocrystalline specimens of [111] and [100] crystallographic orientation were studied. Crystallographic orientations were established by *X*-ray diffractometer DRON-3.

Characteristics of electrophysical and dynamical mechanical properties and dislocation density of boron doped monocrystalline germanium are presented in Table.

From a comparative analysis it is shown that the absolute value of the shear modulus increased significantly with low concentration of boron. Monocrystalline germanium with high concentration of boron is characterized by a decrease of the shear modulus, though its value is high in comparison with undoped specimens.

Annealing at 600 ºC temperature in vacuum for 5hrs causes decrease of current carriers' concentration of the specimens, accordingly their mobility increases. Sharp increase of the shear modulus was revealed in heavily boron-doped monocrystalline germanium. Subsequent annealing at 800 ºC temperature causes a small increase of current carriers' concentration of the specimens. Increase of their shear modulus is insignificant.

Two regimes of thermal treatment practically do not affect the dislocation density and its distribution in the structure. It is known [2] that thermal treatment can cause significant changes in Cottrell atmospheres, formed by impurity atoms in the proximity of dislocations. At medium temperatures (~600ºC) an increase of concentration of impurities and their complexes in Cottrell atmosphere is possible. Accordingly, blocking of dislocations will be increased. This circumstance causes an increase of the absolute values of structural-sensitive shear modulus. Annealing at higher temperatures (800ºC) causes decomposition of complexes of germanium atoms and technological impurities (0_2, N_2, C), distribution of impurity atoms in crystal volume and decrease of their concentration in Cottrell atmospheres. In these condi-

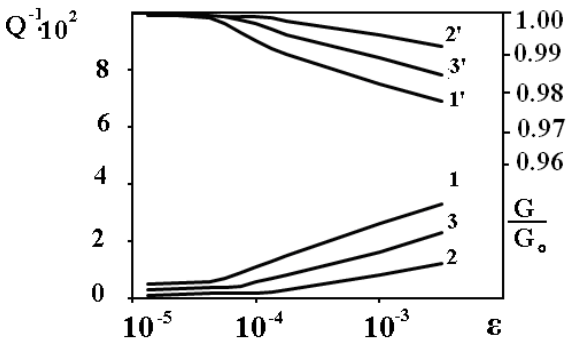

Fig. 1. Internal friction (1, 2, 3) and shear modulus (1′, 2′, 3′) amplitude dependence of boron doped monocrystalline germanium. (1, 2, 3), T=20 ºC. 1,1′ - Ge,[111]; 2,2′ - Ge:B ($1\cdot10^{16}$ cm^{-3}), [111]; 3,3′ - Ge:B ($8\cdot10^{19}cm^{-3}$), [111]

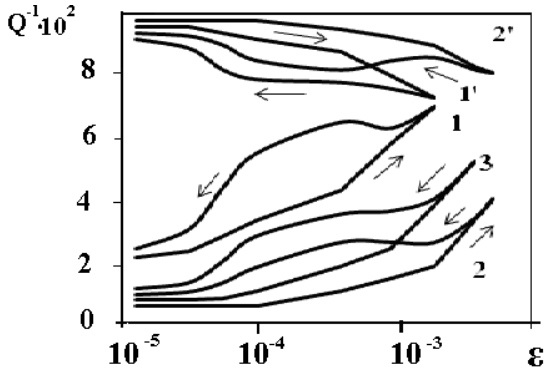

Fig. 2. (Q^{-1}) (1,2,3) and (G/G_0) (1′, 2′) of the monocrystalline Ge:B specimens at 550ºC temperature. 1,1′ - Ge, [111]; 2,22 - Ge:B ($1\cdot10^{16}cm^{-3}$), [111]; 3 - Ge:B ($8\cdot10^{19}cm^{-3}$), [111].

tions a sharp increase of shear modulus is not expectable. It is significant that the nature of thermal treatment effect is similar for the specimens of both [111] and [100] crystallographic orientations.

Internal friction (Q^{-1}) and relative shear modulus (G/G_0) amplitude dependences of boron doped monocrystalline germanium were studied at room temperature, in strain amplitude interval of $1\cdot10^{-5}$-$5\cdot10^{-3}$ (Fig. 1).

Experimental specimens are characterized by critical strain amplitude, at which internal friction intensity begins to increase (Fig.1: 2, 2′) show that weakly doping with boron significantly increases the critical values of strain amplitude. In the case of high concentration of boron, the critical strain amplitude decreases, but it remains much higher in comparison with undoped monocrystalline germanium.

The values of elastic limit were determined with the values of critical strain amplitude and shear modulus. The obtained results are presented in Table. It is experimentally established that weakly boron doped monocrystalline germanium is characterized by high values of elastic limit. In comparison with them, the values of elastic limit of undoped and heavily boron doped germanium are much lower.

Internal friction and dynamical shear modulus amplitude dependences of Ge:B monocrystals are presented in the Fig.2. Measurements were conducted at 550 ºC temperature, at which development of plastic deformation in germanium is possible.

Internal friction and shear modulus amplitude dependences at 550 ºC temperature have a multistage character. Internal friction spectrum of the specimen with [111] crystallographic orientation has three separate ranges. In the first range (5×10^{-6}-7×10^{-4}) internal friction intensity is low and it increases weakly in proportion to the oscillation amplitude. Significant linear increase of internal friction intensity begins at the first critical amplitude up to the second critical amplitude. Internal friction intensity increases with the subsequent increase of amplitude (Fig. 2: 1).

The first critical amplitude corresponds to the critical strain at which breakaway of dislocation segments from the pinning points (vacancy, impurity atoms and complexes) begins. It is known [3] that up to the first critical deformation only bending of dislocation segments takes place. Irreversible increase of internal friction is observed from the second critical amplitude. Anomalous high intensity wide maximum of internal friction is revealed on the return curve.

According to the theory [3], at the second critical amplitude dislocation breakaway begins from the strong pinning centers and their motion. Generation of new dislocations is also possible. After the end of vibrations dislocation segments do not return to the initial state. This means that microplastic deformation takes place, with generation of new dislocations

and breakaway of existing dislocation segments from strong pinning points.

Analogously to undoped specimen, in the internal friction amplitude spectrum of weakly boron doped germanium two values of critical amplitude were revealed (Fig.2: 2). Both of them are increased in comparison with undoped specimens. Internal friction wide maximum was revealed on the return curve registered from the second critical amplitude, which is connected to hysteretic type oscillation energy scattering processes. On the curve of $Q^{-1}(\varepsilon)$, open loop of hysteretic type is revealed, confirming development of microplastic deformation.

The $Q^{-1}(\varepsilon)$ dependence of heavily boron doped germanium is characterized by two critical strain amplitudes. Their values are higher in comparison with undoped germanium, and much lower in comparison with characteristics of weakly boron doped specimens. Changes of the complex character of shear modulus of all specimens take place in a wide range of oscillation amplitude. Two critical points are revealed on the curve of the shear modulus amplitude dependence (Fig.2: 1′, 2′). Microplastic deformation is sharply revealed in the interval of high strain amplitude, in the form of an open loop.

On the basis of the results presented in Fig 2, the values of elasticity limit have been determined. It has been established that weakly boron doped monocrystalline germanium is characterized by high elastic limit, critical strain amplitude and shear modulus. This is due to structure strengthening, being caused by an increase of dislocation blocking by boron atoms.

In the case of high concentration of boron simultaneously with the strengthening process, "softening" process takes place. It is determined by fulfillment of broken electron bonds near to dislocations cores that causes decrease of activation energy of dislocations motion. All this is reflected in the decrease of mechanical characteristics of boron heavily-doped germanium.

Thus, control of changes of electrophysical and mechanical characteristics of the dislocation structure of monocrystalline germanium by boron-doping is possible. This circumstance is significant for the solution of various problems of materials based on germanium.

ფიზიკური ქიმია

ბორით ლეგირებული მონოკრისტალური გერმანიუმის დინამიკური მექანიკური თვისებები

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ნაშრომში გამოკვლეულია ბორით ლეგირებული მონოკრისტალური გერმანიუმის მიკროსტრუქტურა, ელექტროფიზიკური თვისებები, დინამიკური ძვრის მოდულისა და მიკროპლასტიკური

დეფორმაციის მახასიათებლები. გერმანიუმის მასიური კრისტალები გაზრდილია ჩოხრალსკის მეთოდით [111] კრისტალოგრაფიული მიმართულებით. მონოკრისტალებში ბორის კონცენტრაცია იცვლება $5\cdot10^{16}$–$5\cdot10^{19}$ სმ$^{-3}$ ინტერვალში. მოწამვლის ორმოების რაოდენობის შეფასებით განსაზღვრული დისლოკაციების სიმკვრივე იცვლება 10^3-დან $5\cdot10^4$ სმ$^{-2}$-მდე. დადგენილია, რომ ბორის კონცენტრაციის გაზრდით მცირდება დენის მატარებელი ხვრელების ძვრადობა და იზრდება დინამიკური ძვრის მოდულის აბსოლუტური მნიშვნელობა არალეგირებულ მონოკრისტალურ გერმანიუმთან შედარებით. მაღალტემპერატურული მოწვის შემდეგ ვლინდება დენის მატარებლების ძვრადობის, დინამიკური ძვრის მოდულისა და დრეკადობის ზღვრის ზრდის ტენდენცია.

ბორით ლეგირებული მონოკრისტალური გერმანიუმის შინაგანი ხახუნისა და ძვრის მოდულის ამპლიტუდური დამოკიდებულების შესწავლით მიიღება შემდეგი შედეგები: განსაზღვრულია სხვადასხვა შედგენილობის Ge:B მონოკრისტალების კრიტიკული ამპლიტუდური დეფორმაციის, დინამიკური ძვრის მოდულისა და დრეკადობის ზღვრის მნიშვნელობები. დადგენილია, რომ ბორით სუსტად ლეგირებული მონოკრისტალური გერმანიუმი ხასიათდება ძვრის მოდულის, კრიტიკული ამპლიტუდური დეფორმაციისა და დრეკადობის ზღვრის მაღალი მნიშვნელობებით. ეს გარემოება განპირობებულია გერმანიუმის სტრუქტურის განმტკიცებით, რასაც იწვევს ბორის ატომებით დისლოკაციების ბლოკირების გაძლიერება. ბორის მაღალი კონცენტრაციების შემთხვევაში განმტკიცების პროცესთან ერთად მიმდინარეობს "დარბილების" პროცესი. ეს უკანასკნელი გამოწვეულია ელექტრონული გაწყვეტილი კავშირების შეკვსებით დისლოკაციების ბირთვების მახლობლობაში, რაც თავის მხრივ განაპირობებს დისლოკაციების მოძრაობის აქტივაციის ენერგიის შემცირებას. დისლოკაციებისა და ბორის ატომების ურთიერთქმედების ბუნების ცვლილების გათვალისწინებით გაანალიზებულია ბორის გავლენით სტრუქტურის განმტკიცებისა და "დარბილების" მექანიზმები.

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