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МЕТОД ФУНКЦИОНАЛА ПЛОТНОСТИ В ОПИСАНИИ АТОМНОЙ АВТОИОНИЗАЦИИ ВО ВНЕШНЕМ ЭЛЕКТРИЧЕСКОМ ПОЛЕ: НОВАЯ РЕЛЯТИВИСТСКАЯ СХЕМА

Резюме

В рамках S-матричного формализма Гелл-Мана и Лоу и релятивистской теории возмущений изложена новая релятивистская схема метода функционала плотности для описания характеристик атомной автоионизации во внешнем электрическом и лазерном поле.

Ключевые слова: автоионизация, теория функционала плотности, электрическое поле.

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МЕТОД ФУНКЦИОНАЛУ ГУСТИНИ В ОПИСАНИИ АТОМНОЇ АВТОІОНІЗАЦІЇ У ЗОВНІШНЬОМУ ЕЛЕКТРИЧНОМУ ПОЛІ: НОВА РЕЛЯТИВІСТСЬКА СХЕМА

Резюме

В межах S-матричного формалізму Гелл-Мана та Лоу і релятивістської теорії збурень викладена нова релятивістська схема метода функціоналу густини для опису характеристик атомної автоіонізації у зовнішньому електричному та лазерному полі.

Ключові слова: автоіонізація, теорія функціоналу густини, електричне поле.

INFLUENCE OF IMPURITIES AND DISLOCATIONS ON THE VALUE OF THRESHOLD STRESSES AND PLASTIC DEFORMATIONS IN SILICON

The dependence of a plastic flow stress and deformation values on the presence of clear and precipitated by impurity initial structural defects in epitaxial *p* – silicon without foreign impurity and in epitaxial *p* – silicon with oxygen impurity is investigated. It is established, that, boron doping of silicon is the reason of threshold stress reduction in comparison with threshold stress for clear from defects silicon and leads to reduction of its hardness. Presence of oxygen atoms, precipitating dislocations in plates, stimulates the increase of threshold stress.

1. INTRODUCTION

Structural and impurity defects, their distribution in initial semiconductor plates at technological processing, can make decisive influence on the process of new defects' generation that influences on degradation properties and on percentage yield of devices. In spite of the fact that it has been studied many years, the problem of defects in silicon remains actual till now. First of all, it is connected with the increase of electronic microcircuits integration, and with transition from micro technologies to nano technologies. Many works are devoted to studying recombination active defects arising in the course of silicon crystals cultivation [1]; defects in silicon nanowires [2]; problems of iron gettering in silicon by means of oxygen precipitates [3, 4]; optical attenuation on silicon divacancies [5]; controllable cultivation of dislocations [6]; redistributions of dislocations in silicon [7] and other defect properties.

It is informed [8] that silicon crystals, containing appreciable quantity of oxygen atoms, are the best basis for integrated microcircuits creation, than clearer crystals. Despite of considerable amount of works on this problem [9, 10], a number of questions connected with impurity influence on the stress of the beginning of a plastic flow remain unsolved.

The purpose of given work is the establishment of laws of stresses and relative deformations changes under the influence of structural and impurity variations of silicon plates.

2. OBJECTS AND METHODS OF RESEARCH

We studied epitaxial boron-doped silicon plates of grade BDS 10 (111) with the diameter of 60 mm and thickness of 405 microns.

Following methods and equipment were used for studying defects on a silicon surface:

- a method of selective chemical etching by Sirtle [11];
- scanning electronic microscopy of a surface (SEMS), by means of scanning electronic microscope-analyzer “Cam Scan” – 4D with a system of the energetic dispersive analyzer “Link – 860” (with the usage of “Zaf” program, mass sensitivity of the de-

vice is 0,01 %, beam diameter ranges from $5 \cdot 10^{-9}$ to $1 \cdot 10^{-6}$) [12];

- optical methods of researches with the usage of metallographic microscope “MMP – 2P”;

- OZhe electronic spectroscopy (OES), by means of spectrometer LAS-3000, manufactured by “Riber” (with spatial resolution of 3 microns and energetic permission of analyzer of 0,3 %).

Selective chemical etching was applied to samples before studying of their defects with the usage of metallographic microscope “MMP – 2P” and of electronic microscope “Cam Scan”. For etching of plates with (111) -oriented surface plane Sirtle etchant was used. Its chemical compound is as following: 50 g of CrO_3 + 100 ml of H_2O + 100 ml of HF (46 %). Etching time was from 2 till 15 minutes, etching speed was about 2 – 3 microns/minute. Preliminary processing of plates in Caro and hydrogen-ammonia compositions [13] was made before selective etching. It allowed us to raise revealing properties of selective etchant. The revealed defects looked like dislocational etching poles, lines of dislocations or dislocational grids.

3. RESEARCH AND CALCULATION PECULIARITIES

It is established, that deformations of a rigid body arise under the influence of mechanical stresses. Stress τ dependence on deformation ε is presented on the graph of (fig. 1) [14].

Crystal deformation occurs not only under the influence of external mechanical stresses. Crystal doping, presence of uncontrollable oxygen, carbon, hydrogen impurities and impurities of other elements in the course of cultivation always leads to the change of lattice constant, and, hence, to existence of areas with changed mechanical potential [15]. Elastic stresses in silicon lattice, caused by implantation of atoms of another size, are described by Poisson formula [11]:

$$\tau = \omega \cdot 2\mu \cdot \frac{1+\nu}{1-\nu} \cdot C, \quad (1)$$

with ω – Vegard constant;

$$\nu = -S_{12} / S_{11} \text{ — Poisson constant (tab. 1);} \quad (2)$$

$$\mu = 1/S_{44} \text{ — shear modulus (tab. 1);} \quad (3)$$

C — impurity concentration;

S_{mn} — elastic compliance coefficient [14].

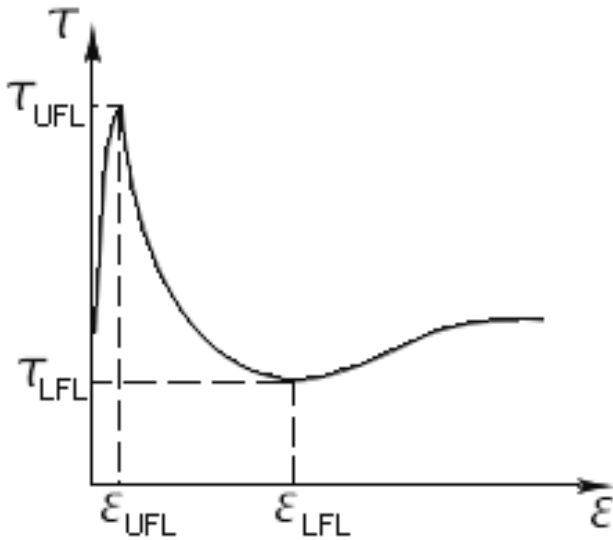


Fig. 1. Typical dependence of $\tau = f(\varepsilon)$ for covalent crystals: τ_{UFL} , τ_{LFL} , ε_{UFL} , ε_{LFL} — shear stresses τ and the deformations ε , corresponding upper fluidity limit (UFL) and lower fluidity limit (LFL).

In the given work the area of plastic flows (from $(\tau_{UFL}, \varepsilon_{UFL})$ to $(\tau_{LFL}, \varepsilon_{LFL})$) on the curve of fig. 1 was investigated. Namely, we studied the value of residual stresses and deformations, arising in a crystal after cancellation of deformation and formation of structural defects. We were not interested in mechanical deformation of a crystal (stretching, compression, blow, bend, cave-in and other), but in initial (internal) deformation which possesses the crystal before exposure to external deformation. This initial deformation of a crystal is formed in the course of growth and subsequent doping. Stresses and deformations brought into a crystal by defects, formed in the course of its growth, were investigated in this work. Useful (doping) impurity as, for example, boron in *p*-silicon and phosphorus in *n*-silicon, as well as any other impurity, refers to the category of point defects.

Table 1

Results of required calculations of critical stresses and deformations, and also intermediate values for clear silicon.

Lattice constant a_0 , Å [18]	5,431	
Vegard constant for boron ω_{boron} [17]	$2,8 \cdot 10^{-3}$	
Vegard constant for oxygen ω_{oxygen} [17]	$1 \cdot 10^{-4}$	
Elastic compliance coefficient, $\frac{m^2}{N}$ [14]	S_{11}	$2,14 \cdot 10^{-12}$
	S_{11}	$7,68 \cdot 10^{-12}$
	S_{44}	$12,6 \cdot 10^{-12}$
Shear modulus M , $\frac{N}{m^2}$ (3)	$7,94 \cdot 10^{13}$	
Poisson constant X (2)	0,28	
Atom concentration C , cm^{-3} [18]	$5 \cdot 10^{22}$	
Critical stress value τ_{UFL} , $\frac{N}{m^2}$ [14]	10^8	
Critical deformation value ε_{UFL} (8)	$1,3 \cdot 10^{-3}$	

For silicon plates, containing dislocations with residual stresses around dislocation cores, the top of fluidity limit achievement comes at smaller stresses, than for crystals without dislocations. Studying a defect picture on a surface of silicon plates, it is possible to define value of these residual stresses and deformations, and, also, concentration of point defects.

After selective chemical etching, two types of defect distribution picture in boron-doped epitaxial silicon plates were found out by means of SEMS. Thereupon the investigated plates were divided into 2 groups. By methods of x-ray and OES analyses it was established, that plates of the second group contain oxygen impurity, and plates of the first group do not contain oxygen atoms. A typical representative of the first group of plates is the plate № 1 (fig. 2) with big period of dislocational grid, consisting of 60° dislocations. A typical representative of the second group of plates is the plate № 2 (fig. 3) with small period of dislocational grid, highly precipitated by oxygen atoms. SEMS analysis with a system of the energetic dispersive analyzer “Link — 860” showed that oxygen atoms are placed not only lengthways of dislocational grid, but also in its lattice sites (spheres on fig. 3).

Dislocational grids considered to be repeating linear defects, density of which is expressed through a number of dislocational lines, crossing a surface of unit area, perpendicular to dislocational lines [16].

After definition of dislocations' amount n from the pictures of plates' surface (tab. 2), we calculated surface density of dislocations, using formula

$$N_{surf.} = \frac{n \cdot \text{image increase}}{\text{image square}}. \quad (4)$$

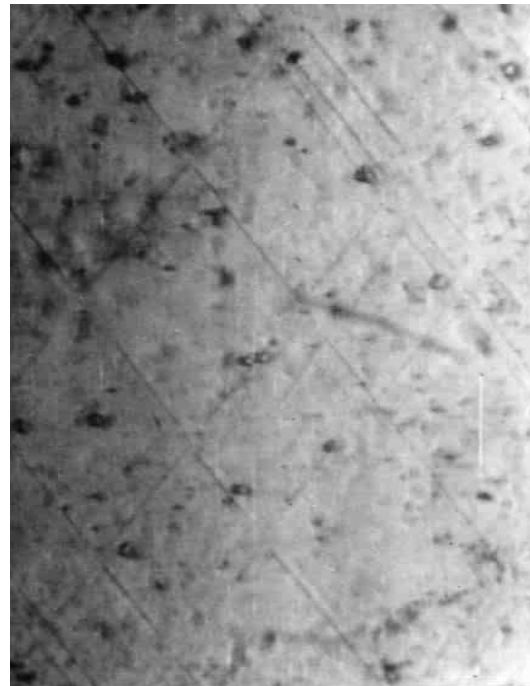


Fig. 2. Image of boron precipitated dislocational grid in *p*-silicon, received after selective chemical etching by Sirtle (depth of analysis $x = 5 \text{ } \mu\text{m}$, image increase is 2300 times, (111) — orientated surface plane).

Value of surface density of dislocations is represented in table 2.

The surface density of dislocations is connected with value of relative deformation ε (tab. 2) and with silicon lattice constant a_0 by a well-known ratio [11]:

$$\varepsilon = \sqrt{a_0^2 \cdot N_{surf.}} \quad (5)$$

Relative deformation, described by Vegard law, arises at the process of impurity diffusion [17]:

$$\varepsilon = \omega \cdot C, \quad (6)$$

with ω — Vegard constant, C — impurity concentration in relative dimensionless units (tab. 2).

In the case of several kinds of impurity resultant relative deformation is defined as the sum of contributions:

$$\varepsilon = \sum_i \varepsilon_i. \quad (7)$$

Shear stress τ_{UFL} and deformation ε_{UFL} in the isotropic structure are connected by ratio [14]

$$\varepsilon_{UFL} = \frac{\tau_{UFL}}{\mu}, \quad (8)$$

with μ — shear modulus (tab. 1).

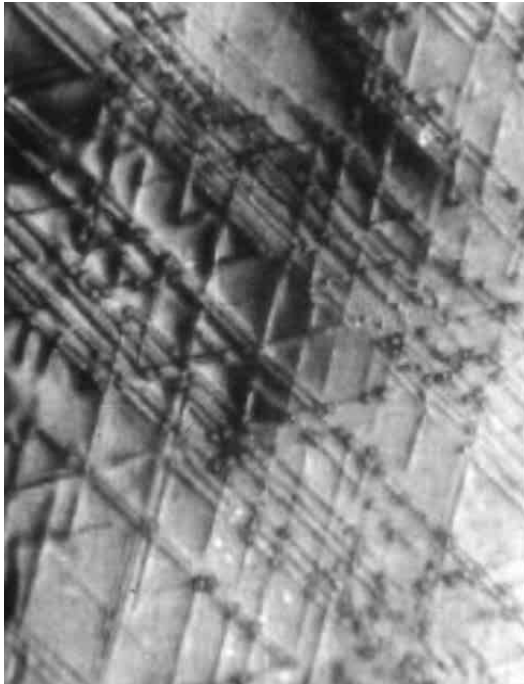


Fig. 3. Image of oxygen precipitated dislocational grid in *p*-silicon, received after selective chemical etching by Sirtle (depth of analysis $x = 5 \text{ mkm}$, image increase is 2300 times, (111) — oriented surface plane).

In the process of dislocation multiplication internal stresses become comparable with external and the real stresses effecting dislocation, will differ from the external. It is considered [14], that the real stresses effecting dislocation are equal to

$$\tau = \tau_{eff.} + \tau_{inn.}, \quad (9)$$

with $\tau_{eff.}$ — external stresses, effecting a crystal, $\tau_{inn.}$ — internal stresses.

Long-range (internal) mechanical stress of uniformly distributed dislocations can be calculated, con-

sidering additive character of internal stresses of each dislocation, according to expression

$$\tau_{inn.} = \alpha \cdot |b| \cdot \mu \cdot N_{surf.}^{1/2}, \quad (10)$$

Here

$$\alpha = 1 - \nu / (2\pi), \quad (11)$$

with ν — Poisson constant (2), $N_{surf.}$ — dislocation density, $|b|$ — Burgers' vector magnitude.

Table 2
Results of stresses and relative deformations calculations, and also intermediate values for the investigated silicon plates

	Plates № 1	Plates № 2
Surface orientation plane	(111)	(111)
Amount n of dislocations on figure, averaged for all plates of one type	17	260
Value of relative deformations in the area of dislocational grids ε (5)	$1 \cdot 10^{-6}$	$2 \cdot 10^{-6}$
Surface density of dislocations $N_{surf.}, \text{ cm}^{-2}$ (4)	357	1320
Stress value in the area of dislocational grids $\tau, \frac{N}{m^2}$ (13)	$9,3 \cdot 10^6$	$1,8 \cdot 10^7$
Concentration of boron impurity $C_{boron}, \%$ (6)	0,04	0,04
Concentration of boron impurity $C_{boron}, \text{ cm}^{-3}$ [18]	$2 \cdot 10^{19}$	$2 \cdot 10^{19}$
Concentration of oxygen impurity $C_{oxygen}, \%$ (6)		0,01
Concentration of oxygen impurity, $C_{oxygen}, \text{ cm}^{-3}$ [18]		$5 \cdot 10^{18}$

As it is seen from fig. 2 and fig. 3, observable dislocational grids consist of 60° dislocations. The Burgers' vector magnitude of 60° dislocations equals to the lattice constant $|b| = a_0$. Introducing the expressions of ε and $\bar{\sigma}$, given by Eqs. (5) and (11) in Eq. (10) one gets:

$$\tau_{inn.} = \frac{1 - \nu}{2\pi} \cdot \varepsilon \cdot \mu. \quad (12)$$

As the surface picture was taken without any external stresses, for $\tau_{eff.}$ one gives: $\tau_{eff.} = 0$. Real stresses, effecting dislocation are equal to internal stress (tab. 2) of uniformly distributed dislocations:

$$\tau = \tau_{inn.} \quad (13)$$

On the other hand, apparently from Eq. (10), the stress, effecting dislocation for lack of external stresses, applied to a crystal, is in direct ratio to a square root from dislocation density.

4. RESULTS AND DISCUSSION

Data, used in presented work and received from the analysis of pictures of a surface and as a result of calculations, averaged for each type of plates, are given in tables 1 and 2. Steams of stress values, received as a result of calculations, and deformations are tabulated for the analysis in table 3.

Table 3
Values of residual stresses and deformations for plates №1 and plates № 2, and also threshold values of stresses and deformations for clear from defects silicon.

	ε	$\tau, \frac{N}{m^2}$
Plates № 1	$1 \cdot 10^{-6}$	$9,3 \cdot 10^6$
Plates № 2	$2 \cdot 10^{-6}$	$1,8 \cdot 10^7$
Threshold values for clear from defects silicon	$1,3 \cdot 10^{-3}$	10^8

As it follows from table 3, residual stresses and deformations for a case of boron-doped silicon (plates № 1) on the curve of fig. 1 are placed more to the left of threshold stresses and deformations for clear from defects silicon that is they correspond to areas of elastic stresses and deformations. It means that in a result of boron precipitation of dislocations the new phase of Si-B was formed. Its threshold of plasticity is more to the left of a threshold of plasticity of clear silicon and, taking into account the formation of dislocations, more to the left of residual stresses and deformations for a plate № 1. Thus, the received values of residual stresses and deformations for a plate № 1 correspond not to silicon, but to Si-B. As the threshold of a plastic flow for this phase is less, than for silicon it is possible to draw a conclusion that in a result of boron doping hardness of silicon plates reduces.

In a case of oxygen presence in boron-doped silicon plates, (plates № 2) residual stresses and deformations are more to the left of threshold stresses and deformations for clear from defects silicon, but more to the right of residual stresses and deformations for a case of plates № 1.

It is experimentally proved, that value of ϕ_{FL} and, hence, of e_{UFL} for germanium monotonously increases with the increase of oxygen concentration [14]. It is informed; that similar results were found out for silicon, only the mechanism of strengthening of these crystals in the presence of oxygen is not investigated up to the end [9].

5. CONCLUSION

The accessory of residual stresses and deformations' values of plates № 1 to areas of elastic stresses and deformations for clear from defects silicon is caused by the fact, that boron atoms have smaller covalent radius (0,08 nanometers) [19] in comparison with covalent radius of silicon atoms (0,1175 nanometers) [19]. As a result the period of silicon crystal lattice increases when boron is placed in lattice sites. It is connected with the fact, that placing of boron atoms in silicon crystal lattice sites leads to lattice compression in the doped area, and, hence, to corresponding stretching of silicon crystal lattice [20]. As a result mechanical stresses leading to existence of stretching area appear in silicon crystal [21]. Therefore at the application of mechanical stresses, smaller, than threshold stresses for clear from defects silicon, the plastic flow is observed in plates № 1. As residual stresses and deformations for plates № 1 are less than threshold values for clear from defects silicon, it is obvious (fig. 1),

that threshold values of stresses and deformations for p — silicon are placed in the area, more to the left of residual stresses and deformations.

In the case of oxygen atoms in lattice sites of silicon crystal, because of larger covalent radius of oxygen atoms in comparison with covalent radius of silicon atoms, compression areas (caused by lattice stretching in the field of oxygen atom placement [22]) will be formed in silicon crystal. Interstitials (both boron and oxygen) in silicon crystal lattice form areas of compression [22]. Strength reduction of plates № 1 justifies to primary placement of boron in silicon lattice sites. Position of residual stresses and deformations for plates № 2 to the right of residual stresses and deformations for plates № 1 (increase of deformation value) is caused by oxygen presence in plates № 2. Concentration of oxygen atoms equal to 0,01 % in plates № 2, is enough for compensation of hardness reduction effect, called by boron presence in the plates [23]. The presented results justify that controllable introduction of oxygen impurity can be used for increase of mechanical hardness of silicon crystals.

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INFLUENCE OF IMPURITIES AND DISLOCATIONS ON THE VALUE OF THRESHOLD STRESSES AND PLASTIC DEFORMATIONS IN SILICON

Abstract

The dependence of a plastic flow stress and deformation values on the presence of clear and precipitated by impurity initial structural defects in epitaxial *p* — silicon without foreign impurity and in epitaxial *p* — silicon with oxygen impurity is investigated. It is established, that, boron doping of silicon is the reason of threshold stress reduction in comparison with threshold stress for clear from defects silicon and leads to reduction of its hardness. Presence of oxygen, precipitating dislocations in plates, stimulates the increase of threshold stress.

Key words: dislocations, threshold stresses, plastic deformations.

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ВЛИЯНИЕ ПРИМЕСЕЙ И ДИСЛОКАЦИЙ НА ВЕЛИЧИНУ ПОРОГОВЫХ НАПРЯЖЕНИЙ И ПЛАСТИЧЕСКИХ ДЕФОРМАЦИЙ В КРЕМНИИ

Резюме

Исследована зависимость величины напряжений и деформаций начала пластического течения от присутствия чистых и преципитированных примесями исходных структурных дефектов в эпитаксиальном *p*- кремнии без сторонних примесей и в эпитаксиальном *p*- кремнии с примесью кислорода. Установлено, что, легирование кремния бором является причиной уменьшения пороговых напряжений по сравнению с пороговыми напряжениями для чистого от дефектов кремния и приводит к уменьшению его прочности. Присутствие в пластинах кислорода, преципитирующего дислокации, стимулирует возрастание пороговых напряжений.

Ключевые слова: дислокации, пороговое напряжение, пластические деформации.

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ВПЛИВ ДОМІШОК І ДИСЛОКАЦІЙ НА ВЕЛИЧИНУ ПОРОГОВОЇ НАПРУГИ І ПЛАСТИЧНОЇ ДЕФОРМАЦІЇ В КРЕМНІІ

Резюме

Досліджено залежність величини напруги і деформації початку пластичної течії від наявності чистих і преципітованих домішками початкових структурних дефектів в епітаксіальному *p*- кремнії без сторонніх домішок і в епітаксіальному *p*- кремнії з домішкою кисню. Встановлено, що, легування кремнію бором є причиною зменшення порогової напруги в порівнянні із пороговою напругою для чистого від домішок кремнію і призводить до зниження його міцності. Присутність в пластинах кисню, преципітуючого дислокації, стимулює зростання порогової напруги.

Ключові слова: дислокації, порогова напруга, пластичні деформації.