UKRAINIAN JOURNAL OF MECHANICAL ENGINEERING AND MATERIALS SCIENCE
Vol. 1, No. 1, 2015

Valentina Kutzova, Olha Nosko, Andrey Sulay
National metallurgical academy of Ukraine, Dnepropetrovsk, Ukraine

THE STRUCTURE, MECHANICAL AND ELECTROPHYSICAL PROPERTIES OF MONOCRYSTALLINE SILICON UNDER INFLUENCE OF CONSTANT MAGNETIC FIELD

Received: May 19, 2015 / Revised: August 12, 2015 / Accepted: September 16, 2015

Abstract. The monocrystalline silicon is one of the most important materials in the view of the fact that it is used in contemporary electronics. The issues concerning silicon processing methods up to now attract a lot of attention of scientists all around the world. From this point of view, the influence of constant magnetic field upon the monocrystalline Czochralski silicon had been studied.

The processing of monocrystalline Cz-Si (alloyed with Zr, Hf, Mg, Al, and unalloyed) in weak constant magnetic field (0.07 Tesla) has been carried out. The influence of weak constant magnetic field on the structure, mechanical and electrophysical properties of silicon, namely, increasing of internal defects density, forming of polycrystalline structure in unalloyed silicon, significant increment of microhardness and considerable degradation of minority carriers time of life has been noted. The qualitative explanations of magneto-stimulated phenomena in studied specimens from the viewpoint of spin-conversion as well as changes of electronic states density in the space-time as well as that of the influence of alloying elements on the critical points of first type phase transitions in silicon have been suggested.

It has been found that using the weak constant magnetic field lets us to manage the properties of silicon by acceleration or slowing the shear and shear-diffusion phase transitions.

Introduction

At present the semiconductor silicon is a one of the most important materials. Owning complex of properties such as the optimal width of band gap, possibility of deep alloying, long lifetime of minority charge carriers as well good processability and prevalence in nature, the silicon is widely used in different branches of technics such as micro- and nanoelectronics, environmentally friendly energetics etc. More than 90% semiconductor devices of all types produce on the basis of silicon.

In the conditions of constant increasing of the requirements to pureness, structure perfectness of silicon crystals and their homogeneousness, is necessary to improve and deepen the knowledge about properties of silicon as well investigate the methods of silicon processing for obtaining a necessary structure.

In contemporary technical literature the articles about investigations the silicon processing methods are found very rare, except alloying and purification of silicon [1]. The mentions about polymorphism of silicon are extremely rare too, although the possibility of silicon thermal processing has been proved [2]. Recently has been revealed an influence of constant magnetic field at the structure, mechanical and electrophysical properties of silicon [3].

The investigations of processing methods the silicon crystals by heating, magnetic field or other types of influences in the perspective can give a possibility of management their structure and properties at the various stages of production (at the present time all properties of semiconductor silicon conditioned by regimes of its growing). New methods of silicon processing may disclose the prospects of use its other attractive properties such as the high hardness, module of Young, compressive strength and chemical resistance.

Problem statement

The importance of research is focused on possibility of management the structure and properties of semiconductor silicon by means of changes in defects density, minority charge carriers time of life, and specific resistance. It should be noted again that regularities of changes in the structure of silicon at the influence of magnetic field remain poorly studied. There are only separate articles devoted to studying of this problem.

According to contemporary data, the magnetic processing is being considered as the method that can cause the effect of structural relaxation and respectively has influence on the structure-sensitive properties of semiconductors.

As well the influence of magnetic field on properties of silicon has great importance since semiconductor devices often work in such conditions.

Thus, studying the influence of constant magnetic field on the structure, mechanical and electrophysical properties of silicon is very important objective.

Analysis of modern information sources on the subject of the article

The analysis and generalization of literature data shows that magneto-sensitive effects which observed in certain paramagnetic materials (silicon is among them) including the magneto-plastic effect (alterations of dislocations movability at imposing external magnetic field) [4] and magneto-mechanical effect (changes in microhardness of material induced by magnetic field) do not occur in perfect crystals, where are no impurity atoms. The relation between influence of magnetic field and occurring of magneto-sensitive effects in silicon crystals explains by presence of impurities. The all aggregation of physical regularities which characterize magneto-sensitive effects in paramagnetic crystals, explains from viewpoint of spin-dependent transitions of electrons during magnetic processing and after it. The spin-dependent transition leads to essential changing in spin configuration in the clusters of structural defects. It is possible that magnetic field promotes an evolution of spin subsystem in the nanoclusters of structural defects.

Statement of purpose and problems of research

The object of research is determining the effect of the magnetic field of structure and properties of monocrystalline silicon. The fundamental problem is a possibility of management of phase transitions in semiconductor silicon by means of magnetic field, with the aim of forming a favorable structure and properties (on account of decreasing the defects density, increasing the minority carriers time of life and thermal stability).

Experimental procedures

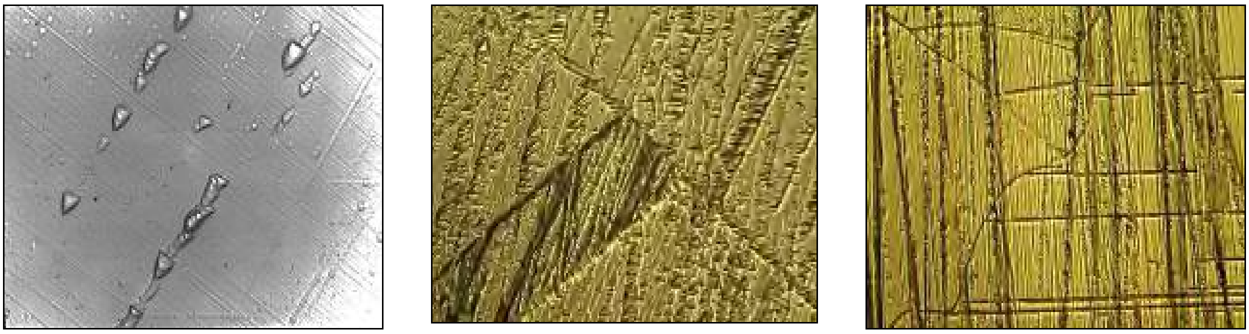
The subject of work was investigation the influence of weak constant magnetic field (magnetic induction 0,07 Tl) at the structure, mechanical and electrophysical properties of alloyed monocrystalline silicon.

As the initial materials have been chosen the specimens of monocrystalline silicon which has been grown by Czochralski method (Cz-Si), unalloyed and alloyed with Hf, Zr, Mg, Al, in quantities from $2*10^{-4}$ to $8,7*10^{-2}$ % at.

The silicon specimens have been processed in the constant magnetic field with induction of 0,07 Tl. The exposition of specimens was 240 and 720 hours. For revealing a structure, specimens were etched in the solution of $HF:H_2O:CrO_3$ in a relation 3:3:1 for 30-60 minutes with further washing in a water. The microstructure has been studied with optical microscope “Neophot-21”. Microhardness of specimens was measured with PMT-3 device at the 20 g loading. The specific resistance was measured by 4-probe method with 2,5% error. Measuring the lifetime of minority carriers has been carried out with GaAs-light emitting diode (SEMILAB WT1000B devise). Precision of device ±0,1%.

Results and discussion

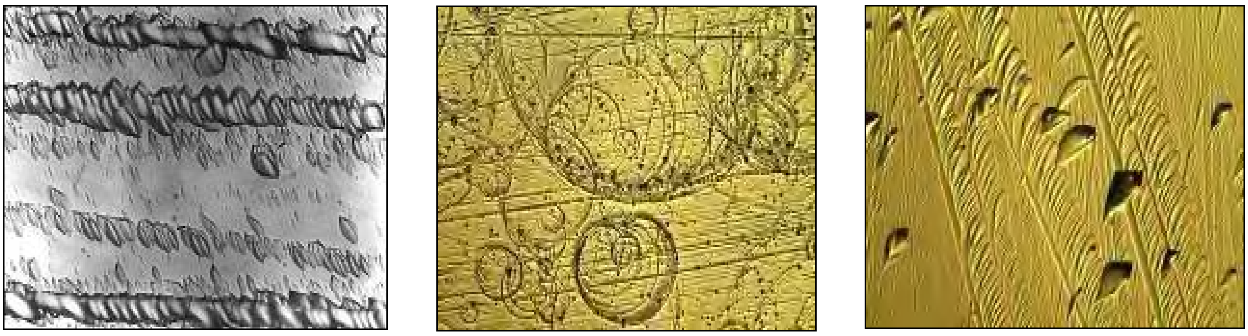
The Fig. 1 shows the microstructure of silicon specimens before and after processing. The initial microstructure is enough homogeneous with low density of dislocations (Fig. 1, a). Exposition of specimens in magnetic field for 10 days was resulted in significant increment of defects density, at first turn – dislocations and forming a large number of twins (Fig. 1, b). The most interesting result of processing was forming of polycrystalline structure as evidenced by presence of grain boundaries. As the dislocations do not change their direction crossing the boundaries, pointed that this is special boundaries. Further exposition in magnetic field does not reflect on the microstructure of specimens (Fig. 1, c).



a) *b)* *c)*

Fig. 1. Microstructure of Cz-Si specimens: a – initial state; b – after 240 hours of exposition; c –after 720 hours of exposition (a – x500; b, c – x400)

The initial microstructure of Cz-Si specimens alloyed with aluminium (Fig. 2, a) has a high density of dislocations. After 240 hours of magnetic processing, in the microstructure was revealed large number of swirl-defects, while the density of dislocations has decreased (Fig. 2, b). Etching of specimens after 720 hours of magnetic processing has revealed small quantities of dislocations (Fig. 2, c).



a) *b)* *c)*

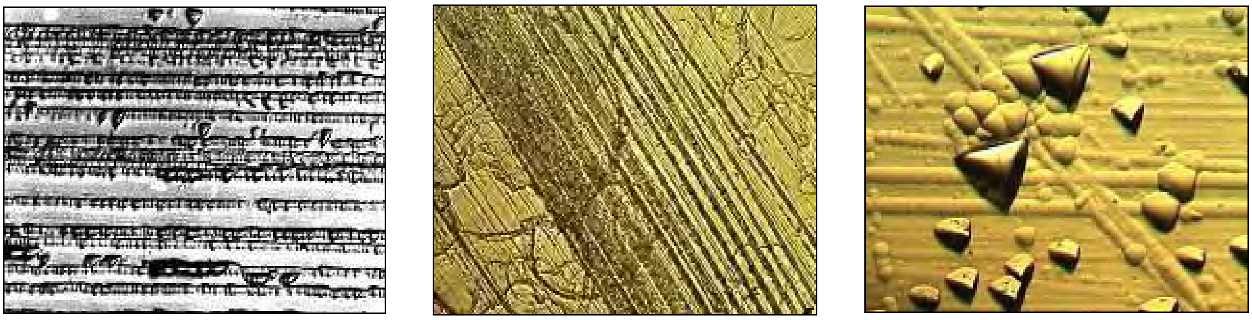
Fig. 2. Microstructure of specimens Cz-Si alloyed with aluminium: a – initial state; b – after 240 hours of exposition; c – after 720 hours of exposition (a – x500; b, c – x400)

In the initial microstructure of Cz-Si specimens alloyed with Zr (Fig. 3) has been observed high density of dislocations (Fig. 3, a) as separated etch pits or their clusters. After magnetic processing for 240 hours the microstructure shows reducing of dislocations density (Fig. 3, b). Metallographic analysis of specimens which have been exposed to magnetic field for 720 hours did not reveal any individual etch pits (Fig. 3, c), the structure of specimens became less defective compared to structure after 240 hours of exposition.

a) *b)* *c)*

Fig. 3. Microstructure of specimens Cz-Si alloyed with Zr: a – initial state; b – after 240 hours of exposition; c – after 720 hours of exposition (a - c – x500)

Fig.4 shows the microstructures of Cz-Si specimens alloyed with hafnium. The initial microstructure characterized by high dislocation density with their regular arrangement along defined crystallographic planes (Fig.4 a). Etching of specimens after 240 hours of exposition has revealed a large number of swirl-defects, while the dislocation density has decreases (Fig.4 b). Significant changes occurred in the microstructure of specimens which have exposed to magnetic field for 720 hours (Fig.4 c), namely: swirl-defects and chains of dislocations have not revealed, but appeared a large number of separate dislocations (in the form of etch pits). Defects density became less in contrast to 240 hours of exposition.



a) *b)* *c)*

Fig. 4. Microstructure of specimens Cz-Si alloyed with Hf: a – initial state; b – after 240 hours of exposition; c – after 720 hours of exposition (a – x500; b, c – x400)

The microstructure of Cz-Si(Mg) specimens, which have been exposed for 240 hours (Fig.5 b) practically has not changed in compare to initial state (Fig.5 a), but after 720 hours of exposition the structure reveals a great number of individual dislocations as etching pits (Fig.5 c).

a) *b)* *c)*

Fig. 5. Microstructure of specimens Cz-Si alloyed with Mg: a – initial state; b – after 240 hours of exposition; c – after 720 hours of exposition (a – x1000; b, c – x400)

The probable reason of forming the large number of twins is formation the rhombic phase of silicon by the shear mechanism [7]. Circumstance that in the unalloyed silicon, shear phase transition $Si_{FCC}\leftrightarrow Si_{RHOMBIC}$ occurs at 350ºC (Table 1) says that in that occasion it conditioned by the influence of magnetic field.

After 720 hours of exposition significant changes in microstructure of specimens were not observed, while a measurement showed increment of microhardness and specific resistance in comparison with them after 240 hours of magnetic processing. This indicates a further passing of phase transition and stabilization of structure under influence of magnetic field. Traces of phase transitions in the structure of silicon alloyed with Al, Zr, Hf, and Mg at magnetic processing were not observed, but defects density was significantly increased.

All of alloying elements which have mentioned above, cause lifting the critical temperatures of phase transitions ($Si_{FCC}\leftrightarrow Si_{RHOMBIC}$ and $Si_{RHOMBIC}\leftrightarrow Si_{BCC\ III}$) in silicon (table 1) and possibly increase thermodynamic stability of these phases to an influence of magnetic field (it is known that magnetic field as the temperature rise, brings additional energy into the system). Also the alloying elements stabilize high-temperature Si_{BCCIII} phase of silicon thereby excluding low-temperature share-diffusion phase transitions and forming of twins in the structure.

Table 1

Temperatures of phase transitions in the silicon and respective values of thermal expansion coefficient

Cz-Si/alloying element	Temperature/ thermal expansion coefficient $^0C/\alpha{\cdot}10^{-6}{\cdot}{}^0C^{-1}$		
	I $Si_{FCC} \leftrightarrow Si_{RHOMBIC}$	II $Si_{RHOMBIC} \leftrightarrow Si_{BCC\ III}$	III $Si_{BCC\ III} \leftrightarrow Si_{HDP}$
Cz-Si	350/4,3	700/4,4	900/5,3
Cz-Si/Al	450/5.0	750/4,5	900/6.0
Cz-Si/Zr	500/4.5	–	850/4.7
Cz-Si/Hf	380/4.5	–	850/4.7

It is known, that aluminium strongly reduces binding energy of silicon atoms and facilitates the shear and shear-diffusion phase transitions in silicon, hafnium on the contrary – significantly increases the binding energy (Fig. 6), i.e. slows passing of phase transitions and stabilizes Si_{FCC} phase.

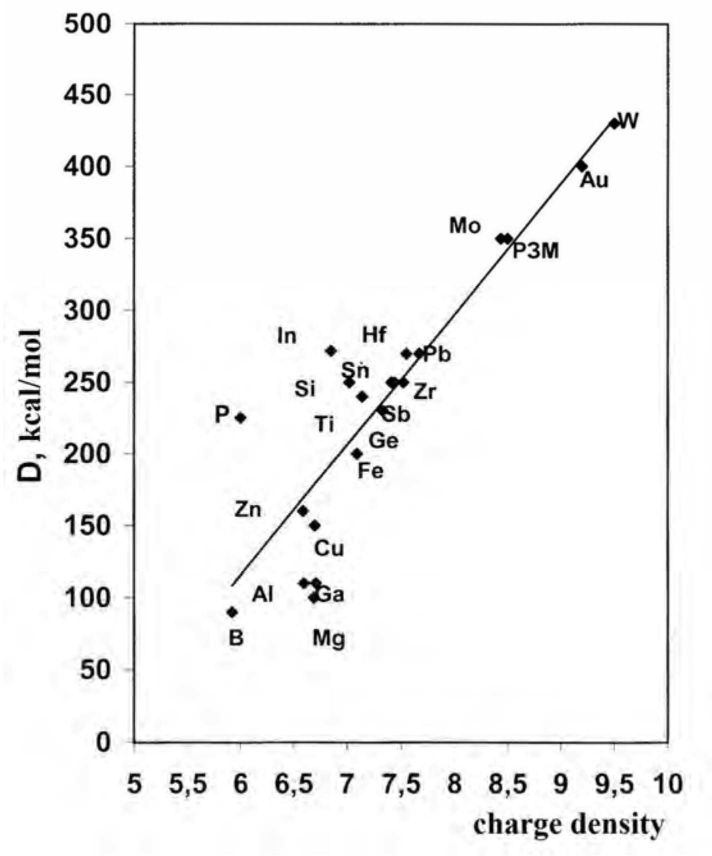


Fig. 6. Correlation of binding energy (D, kcal/mol) and charge density (ρ_l) for interatomic distance which corresponds lattice of silicon at the dissolution of different alloying elements [8]

But as determined in this work, structural changes in the specimens Cz-Si(Al) and Cz-Si(Hf) under influence of constant magnetic field virtually the same (Fig.2 and Fig.4 respectively). This lets to suggest that processing in the magnetic field eliminates the influence of alloying elements on a binding energy of silicon atoms and inhibit the phase transitions.

In the specimens of alloyed silicon, after processing for 240 hours, increment of defects density can be explained by changing the wave functions of electrons. Quite local change of electron's wave functions and restructuring of the crystal lattice will be causing break of covalent bond with neighboring electrons whose wave functions has changed insufficiently for rearrangement of covalent bond orientation (electronic states density in the space-time). This local breaking of bond between atoms will lead to emergence of full dislocation or partial dislocation with a stacking fault.

The average values of microhardness of structural components of the samples are listed in Table 2.

Analysis of table 2 shows that alloying elements, irrespective to their influence on the binding energy between silicon atoms, cause increase (in different degrees) averages of microhardness of structural components of the studied specimens after magnetic processing for 240 hours.

Table 2

The averages of microhardness of structural components of the studied specimens

Specimen	Exposition duration / microhardness, MPa							
	Initial state		240 hours			720 hours		
	matrix	dislo-cations	matrix	dislo-cations	twins/ swirl-defects	matrix	dislo-cations	twins
Cz-Si	6500	5600	9710	9550	12020/-	9880	11555	10600
Cz-Si(Al)	6400	5500	11220	12670	-/10020	8780	11760	−
Cz-Si(Mg)	7150	6250	8940	11000	-/-	9420	11810	−
Cz-Si(Zr)	7250	7500	10000	12570	-/-	8680	10475	−
Cz-Si(Hf)	7750	7400	9030	12460	-/11030	10420	12710	−

Such results of changes in microhardness are in good correlation with results of microstructural analysis, and as it was suggested above, the magnetic processing for 240 hours eliminates the influence of alloying elements on binding energy between silicon atoms, slows phase transitions and stabilizes high-temperature Si_{BCCIII} phase.

Other dependence of changes in microhardness of structural components of the studied specimens is observed after 720 hours of exposition in the magnetic field. The mean values of microhardness the matrix as well structural defects grow in the specimens of unalloyed silicon and specimens alloyed with magnesium and hafnium. On the contrary, reducing the mean values of microhardness the matrix and internal defects is observed in the specimens of silicon alloyed with aluminum and zirconium. Thus, the influence of magnetic field after 720 hours not only eliminates the influence of alloying elements on binding energy, but facilitates shear and shear-diffusion mechanisms of phase transitions in silicon.

Continuous reducing of defects density and microhardness of Si-Al and Si-Zr specimens after exposition for 720 hours in magnetic field can be explained by a stabilization of structure during long exposition in magnetic field and reducing of heat-content of system (enthalpy) by means of annihilation of certain part of defects. Such changes can be observed in the specimens during heat-treatment in the furnace.

At the production of semiconductor devices, the lifetime of minority charge carriers in silicon is a one of the most important characteristics. As is known [9] electrophysical properties, namely, lifetime of minority charge carriers and specific resistance are structural-sensitive parameters.

The values of electrophysical parameters of alloyed and unalloyed silicon specimens before and after magnetic processing are listed in table 3.

Analysis of table 3 shows reducing of electrophysical parameters of all studied specimens, but it is necessary to mention that its character is different. Degradation of electrophysical properties of studied specimens after exposition in the constant magnetic field is in correlation with changes of a microstructure in studied specimens. Forming of polycrystalline structure in the unalloyed silicon after magnetic processing for 240 and 720 hours explains sharp falling of lifetime the minority carriers in three times.

Similar dependency, but with less sharp degradation of electrophysical parameters is observed in Cz-Si(Al) and Cz-Si(Mg) specimens, at this aluminum and magnesium reduce binding energy of silicon atoms in ten times. Exposition of specimens alloyed with elements which increase the binding energy – Zr and Hf – leads to reducing of electrophysical parameters in 2,5 - 6 times.

The reducing of lifetime the minority charge carriers can depends on oxygen content in the surface layers of silicon. As it shown in works [3, 10], during the magnetic processing, in the surface layers of material the oxygen content is highly increases, as well the concentration of alkaline metals ions (K^+, Na^+), hydroxyl groups, and other radicals, that associated with activation of surface and amplification of its adsorption activity under influence of weak constant magnetic field. The oxygen in its ground state (triplet) and radical groups that adsorbed on the surface of silicon, have a capability to seize the minority charge carriers [5], and substantially reduce their lifetime.

Table 3

Electrophysical parameters of alloyed silicon specimens after exposition in the constant magnetic field

Specimen	Electrophysical parameters	Initial state	240 hours of exposition	720 hours of exposition
Cz-Si	ρ, Ohm*cm	80-100	$(46\text{-}49)\times10^{-5}$	$(836\text{-}925)*10^{-6}$
	τ, μs	574	0,65	0,63
	conductivity type	p	p	p
Cz-Si-Al	ρ, Ohm*cm	200-210	55-65	60-65
	τ, μs	12,1-12,5	0,40	0,32
	conductivity type	p	p	p
Cz-Si-Hf	ρ, Ohm*cm	180-192	12,8-14,3	13,5-14,0
	τ, μs	148	23,08	28,11
	conductivity type	p	p	p
Cz-Si-Mg	ρ, Ohm*cm	170-190	44,8-46,2	43,7-50,0
	τ, μs	134-138	16,32	14,55
	conductivity type	p	p	p
Cz-Si-Zr	ρ, Ohm*cm	308-324	13,0-23,5	22,5-25,6
	τ, μs	228	93,3	69,57
	conductivity type	n	n	n

Alloying of silicon with elements which have a higher affinity to oxygen – Zr, Hf, Mg, Al (sequence of affinity the elements to oxygen in descending order) – is likely can reduce the oxygen influence onto the minority carriers time of life through tying its ions with formation of oxides. This is a probable reason of fact that specimens alloyed with listed elements, at the high microhardness have comparably high values of lifetime the minority carriers (excluding Si(Al)).

Conclusions

The magnetic processing of monocrystalline Cz-Si (alloyed and unalloyed), in weak constant magnetic field (0.07 Tesla) has been carried out.

The influence of weak constant magnetic field on the structure, mechanical and electrophysical properties of semiconductor silicon, namely, increasing of density of the internal defects, forming of polycrystalline structure in the unalloyed silicon, significant increment of microhardness and considerable degradation of minority carriers time of life has been noted.

The qualitative explanations of magneto-stimulated phenomena in studied specimens from the viewpoint of spin-conversion, changes of electronic states density in the space-time and the influence of alloying elements on the critical points of first type phase transitions in silicon have been suggested.

It was found that using a weak constant magnetic field, it is possible to manage the properties of silicon by means of acceleration, or slowing the shear and shear-diffusion phase transitions.

References

[1] Случинская И. А. Основы материаловедения и технологии полупроводников / И. А. Случинская. – Москва, 2002. – с. 211–216.

[2] Куцова В. З. Влияние легирования и термической обработки на структуру и свойства полупроводникового кремния / В. З. Куцова, О. А. Носко, А. М. Сулай // Металлургическая и горнорудная промышленность, № 6 (2014) С. 65–72.

[3] Макара В. А. Вплив магнітної обробки на мікротвердість та структуру приповерхневих шарів кристалів кремнію / В. А. Макара, М. О. Васильєв, Л. П. Стебленко // Фізика і хімія твердого тіла. – Том 10, № 1 (2009) С. 193–198.

[4] Скворцов А. А. Влияние слабого магнитного поля на подвижность дислокаций в кремнии / А. А. Скворцов, А. М. Орлов, Л. И. Гончар // Журнал Экспериментальной и Теоретической Физики. 2001. – Том 120. Выпуск 1(7). – с.1601–1607.

[5] Зельдович Я. Б. Магнито-спиновые эффекты в химии и молекулярной физике / Я. Б. Зельдович, А. Л. Бучаченко, Е. Л. Франкевич // Успехи Физических Наук, 155 (1), С. 3–45 (1988).

[6] Урусовская А. А., Эффекты магнитного воздействия на механические свойства и реальную структуру немагнитных кристаллов / А. А. Урусовская, В. И. Альшиц, А. Е. Смирнов, Н. Н. Беккауэр // Кристаллография, 48 (5), С. 855–872 (2003).

[7] Червоний І. Ф. Напівпровідниковий кремній / І. Ф. Червоний, В. З. Куцова, О. А. Носко. – Запоріжжя: Запорізька Державна Інженерна Академія, 2009. – 446 с.

[8] Носко О.А. Особенности структуры, фазовые превращения легированного кремния и модифицированных заэвтектических силуминов и разработка способов повышения их свойств / О. А. Носко // Диссертация на соискание ученой степени кандидата технических наук. – Днепропетровск. – 2006. – 215 с.

[9] Рейви К. Дефекты и примеси в полупроводниковом кремнии. – Москва : Мир, 1984. – 472 с. С.134–138.

[10] Левин М. Н. Активация поверхности полупроводников воздействием импульсного магнитного поля / А. В. Татаринцев, О. А. Косцова, А. М. Косцов // Журнал Экспериментальной и Теоретической Физики. 2003. – Том 73. – № 10. – С. 85–87.