PECULIARITIES OF THE DEFECT FORMATION IN THE NEAR-SURFACE LAYERS OF Si SINGLE CRYSTALS UNDER ACOUSTOSTIMULATED IMPLANTATION OF IONS OF BORON AND ARSENIC

O.I. GUDYMENKO, V.P. KLADKO, V.P. MELNIK, YA.M. OLIKH, V.G. POPOV, B.M. ROMANYUK, M.V. SLOBODIAN, P.P. KOGUTYUK

V.E. Lashkarev Institute of Semiconductor Physics, Nat. Acad. Sci. of Ukraine
(41, Nauky Ave., Kyiv 03028, Ukraine; e-mail: kladko@isp.kiev.ua)

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We study the peculiarities of the transformation of point defects and elastic deformations in the near-surface layers of silicon implantated by B^+ and As^+ ions under the simultaneous *in situ* action of ultrasound (US). As a method of study of a structural perfection of implanted structures, we used multi-crystal X-ray diffractometry. By secondary-ion mass-spectrometry, we determined the thickness distributions of the implanted impurities after the thermal annealing and studied the influence of the US treatment on them. It is shown that the implantation of B^+ into Si samples increases the mechanical stress in the near-surface regions of a wafer. The additional action of US on the implantation causes not only some decrease in stress, but also changes the deformation sign, which is due to both the redistribution of point defects and the variation of their sizes. The annealing of samples at $T = 800 \div 950$ °C induces the stress relaxation in the initial samples and in the implanted ones irrespective of the ions type, and the action of US stimulates this process of relaxation yet more. A physical model of the discovered effects is proposed.

1. Introduction

The implantation of various ions is used in the technology of superlarge integrated circuits for the formation of alloyed p^+- and n^+-regions [1,2]. On the implantation, the point defects, whose concentration depends on the type of ions and the mode of implantation, are generated. After the high-temperature annealing which is used for both the elimination of radiation-induced defects and the electric activation of an alloying impurity, the secondary defects in the form of interstitial dislocation loops and the precipitate of an impurity are formed [3]. The presence of defects and the difference in the covalent radii of atoms of the matrix and alloying impurities cause the appearance of mechanical stresses which influence the diffusion of impurities, the course of quasichemical reactions in the region of the distribution of an implanted impurity, and the characteristics of structures and devices.

The introduction of US into a crystal during the implantation (*in situ*) modifies the physical processes of the formation of defects in a crystal, which is implanted and is in a nonequilibrium state, and can significantly affect the further course of these changes during the annealing [4]. It was shown in [5] that the introduction of US oscillations into a Si wafer in the process of implantation causes the spatial separation of point defects, which influence both the activation of alloying impurities and the accumulation of residual defects. The acoustostimulated processes of relaxation of elastic deformations in the process of ion implantation into SiGe structures were investigated in [6].

Multi-crystal X-ray diffraction is widely applied to the study of a structural perfection of crystals and complex structures after the implantation of various ions [7, 8] and gives information about the distribution of the mechanical fields of deformations and defects.

The purpose of the present work is to study the influence of the action of US in the process of implantation of ions B^+ and As^+ on the transformation of the system of point defects and elastic deformations in near-surface layers of silicon.

2. Experimental Procedure

The implantation of ions B^+ or As^+ with an energy of 35 keV was performed at $T = 20$ °C in a dose interval 10^{15}–10^{16} cm^{-2}. Simultaneously, we implanted the control sample (without US treatment) and a sample with US treatment. The longitudinal US wave (a frequency of 9 MHz and an intensity of 1 W$\cdot$cm^{-2}) was excited with the use of a $LiNbO_3$ piezoelectric transducer positioned on the rear side of a Si plate covered by a liquid binder. After the implantation, the plate was cut into parts, and they were annealed in the Ar atmosphere in a temperature interval $T_{\text{anneal}} = 800 \div 900$ °C for 3 min.

Profiles of the distribution of impurities were determined by the method of secondary-ion mass-spectrometry on an INA-3 setup (Leybold, Germany). We used the mode of high-frequency sputtering of the sample by ions Ar^+ (500 eV) at a frequency of 50 kHz and an on-off ratio of 0.6.

The perfection of a crystal and the level of deformations in structures were studied by the method of X-ray diffractometry. The measurement of X-ray rocking curves was carried out by the method of two-crystal diffractometry for different geometries (a symmetric tangent corresponded to reflection 400, and an asymmetric one did to reflections of the 113 type). In the first case, we tested a deeper near-surface region of a crystal (~ 5 μm), than that in the second one (~ 1 μm) [9]. We used the characteristic emission of an X-ray tube with a copper anticathode (a wavelength of 0.154 nm).

The difference of interplanar distances $\Delta d = d_f - d_s$ depends on the types of a film and the substrate, values of deformations, and orientation of atomic planes. Here, the indices f and s are referred to the implanted layer and the substrate, respectively.

Deformations both normal ($\varepsilon_\perp$) and parallel ($\varepsilon_\parallel$) to the crystal surface are determined in elasticity theory by the relative change of interatomic distances in the substrate and the implanted layer:

$$\Delta d/d_s = \varepsilon_\perp \cos^2 \Psi + \varepsilon_\parallel \sin^2 \Psi, \qquad (1)$$

where Ψ is the angle between the planes and the crystal surface.

The differential angle $\Delta\omega$ is equal to

$$\Delta\omega = \vartheta - \vartheta_\mathrm{B} + (\varepsilon_\perp \cos^2 \Psi +$$

$$+\varepsilon_\parallel \sin^2 \Psi)\mathrm{tg}\vartheta_\mathrm{B} \pm (\varepsilon_\perp + \varepsilon_\parallel) \sin\Psi \cos\Psi, \qquad (2)$$

where ϑ_B and ϑ are, respectively, the Bragg angle and the grazing incidence angle of X-rays. Thus, by measuring two components of a deformation, we can calculate the degree of the relaxation of mechanical stresses in the given structure.

The structural perfection (the concentration and sizes of point defects) was estimated from the analysis of the distribution of the diffuse component of the intensity of X-rays which is manifested on the tails of the reflection curves [9,10]. The analysis of the angular distribution of the diffuse scattering allows us to estimate not only the size of point defects, but to analyze a symmetry of deformation fields and to determine the type of a defect: the vacancy or interstitial one.

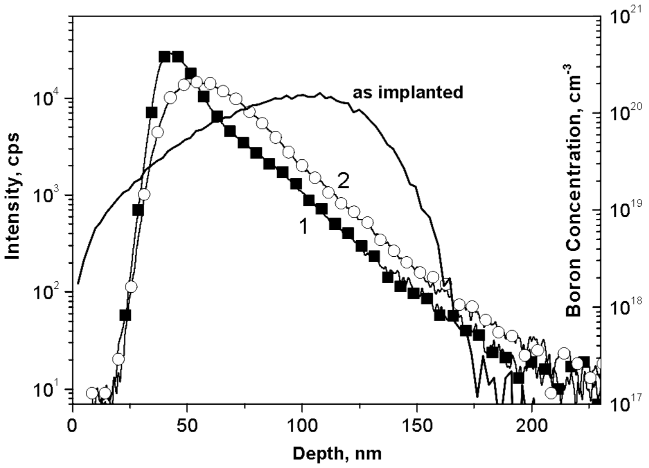


Fig. 1. Profiles of the distribution of implanted ions of boron in a Si crystal: *1*) without US treatment; *2*) with US treatment

3. Results of Experiments

In Fig. 1, we present the profiles of the distribution of atoms of boron implanted into Si without and with the action of US after the annealing at a temperature of 800 °C for 3 min. We also give the distribution of implanted atoms of boron before the annealing (for both cases of the implantation with and without US treatment).

As seen from Fig. 1, the profiles of the distribution in annealed samples differ from each other. In the structures implanted without the action of US, the profile is positioned closer to the surface, and the concentration of boron at the maximum is twice greater as compared with that in the sample implanted with the action of US. This testifies to the segregation of an impurity in the sample implanted without US.

In Fig. 2, we present the profiles of the distribution of atoms of arsenic in the structures implanted without (*1*) and with the action of US (*2*) after the annealing at a temperature of 900 °C for 3 min. It is seen that a significant part of As is accumulated near the surface. The effect of accumulation is more pronounced in the structures implanted under the action of US. In these samples, we also observe a decrease in the concentration of the impurity in a region of 25–60 nm.

In Fig. 3, we show the X-ray diffraction spectra for reflection 400 in the samples implanted with ions B^+ (*a*) and As^+ (*b*) without US and with US treatment before the annealing.

As follows from Fig. 3, the diffraction rocking curves (DRCs) for a crystal implanted with boron with US

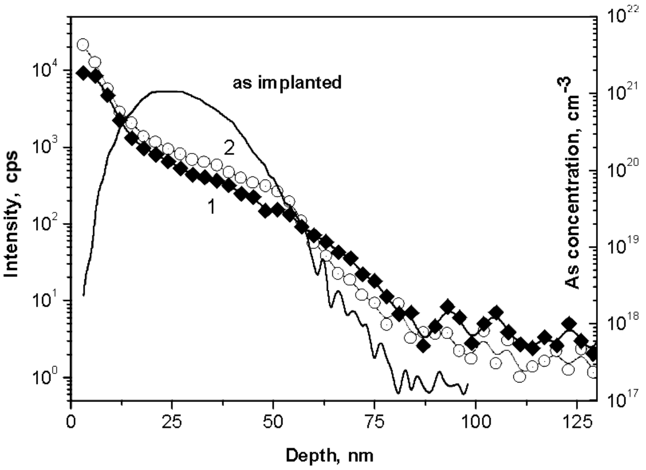


Fig. 2. Profiles of the distribution of implanted ions of arsenic in a Si crystal: *1* without US; *2* with US treatment

treatment differ strongly from those in the case where the implantation occurs without US treatment. In the crystal implanted with US treatment, the DRC demonstrates a high asymmetry which is manifested in the presence of a shoulder from the side of great Bragg angles. This testify that, during the action of US, the profile of the lattice constant is changed over depth stronger than in the case without US. The sign of a deformation corresponds to the vertical compression of the lattice (the maximum deformation of compression $\varepsilon = -2.4 \times 10^{-4}$).

For the samples alloyed by ions of arsenic, the difference between a sample subjected to the US treatment and the standard one is less significant, though it repeats the dependence for boron in general features (Fig. 3,*b*).

After the annealing, the pattern changes to the opposite side: the growth of the diffuse scattering is revealed from the side of less angles (a tension of the lattice). As was mentioned above, these spectra correspond to the symmetric reflection (the depth of penetration of X-rays is about 5 μm) and, thus, contain mainly the information about the transformation in deeper near-surface regions.

DRCs for the asymmetric reflection 113 before the annealing are given in Fig. 4. The analysis of these data shows that the asymmetry of the swinging curves for the samples alloyed with boron is shifted to the side of less angles for all samples. This testifies that the regions of a crystal close to the surface are in the state of tension (the deformation $\varepsilon = 1.04 \times 10^{-4}$). The annealing leads to a further increase of the diffuse scattering in the region of smaller angles and to an increase of tensile stresses ($\varepsilon = 1.75 \times 10^{-4}$). For the samples alloyed with ions of arsenic, the increase of the intensity of the diffuse scattering in the region of greater angles is observed for both geometries of measurements. However, we note that the asymmetry of DRCs can be caused also by an increase in the diffuse component of the reflection due the presence of point defects.

In the Table, we give the dependence of the size of microdefects of the dominant type in crystals implanted with arsenic on the annealing temperature. The analysis of these data indicates that the size of defects passes through a minimum. It is worth to note that the sizes of defects in the samples with US treatment are less in the whole temperature interval under study.

The type of defects is determined by the law of decrease of the field of deformations with increase in the reflection order (the square law for defects of the cluster type and the 3/2-law for dislocation loops) [11, 12].

By using DRCs constructed in logarithmic coordinates, we determined the mean sizes of the coagulates of point defects by the transition point from the Huang law of of decrease of the intensity of the diffuse scattering to the asymptotic law [13–15].

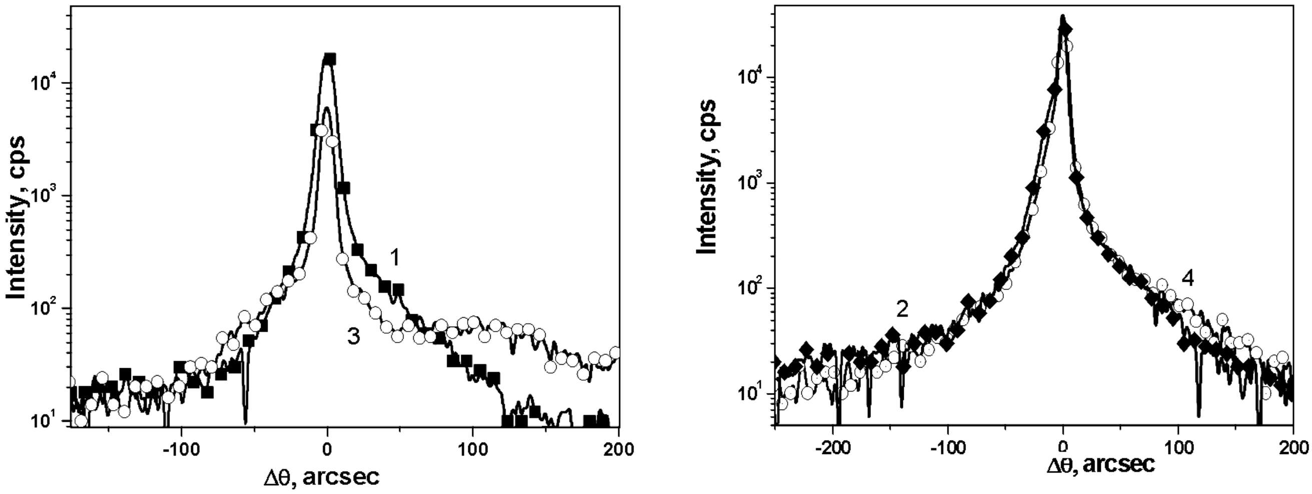
4. Discussion of Results

The implantation of ions As$^+$ and B$^+$ leads to the additional compressive stresses in the structure, and the interplane distance in a film increases normally to the surface. The effect of the increase in stresses is proportional to the implantation dose. These effects are well known and described in the literature [16, 17].

On the implantation of light ions (boron), separate point defects and small disordered regions are formed in Si. No amorphous phase is created at the B implantation doses used in the present work. In the implanted samples without US treatment (without annealing), we did not observe a widening of DRCs for the symmetric reflection 400 relative to those for a nonimplanted

Dependence of the mean size of defects and the maximum values of deformations ε in Si alloyed with ions B$^+$ and As$^+$ on both the treatment mode in the process of implantation and the temperature of a further annealing

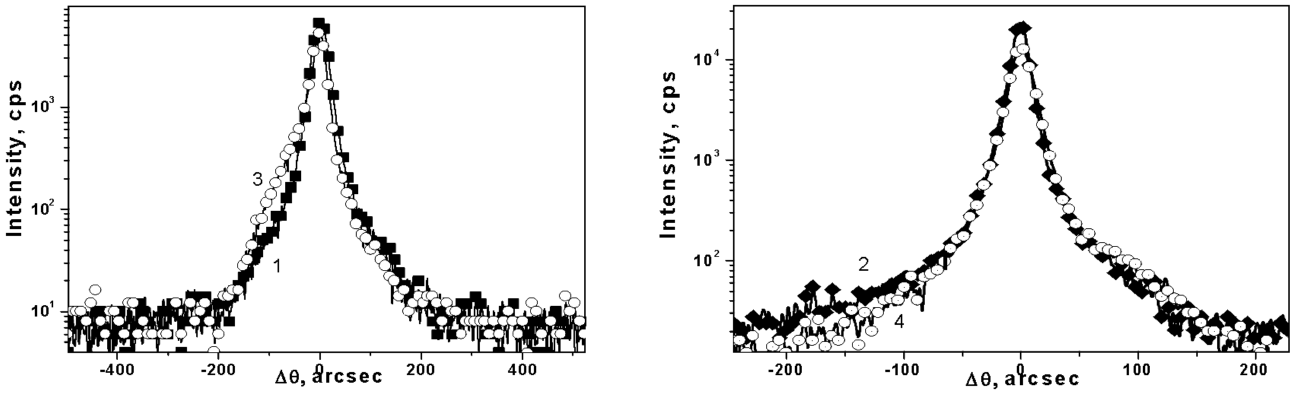
T_{anneal}, °C	US	r_{B}, nm	r_{As}, nm	$\varepsilon_{\text{B}}^{\max}$	$\varepsilon_{\text{As}}^{\max}$
Without annealing	0	–	726	-1.34×10^{-4}	–
Without annealing	+	615	611	-2.4×10^{-4}	–
800	0	745	965	1.75×10^{-4}	0.48×10^{-4}
800	+	868	800	1.04×10^{-4}	0.27×10^{-4}
900	0	–	719	–	0.5×10^{-4}
900	+	–	440	–	0.2×10^{-4}



a

b

Fig. 3. Diffraction rocking curves for the symmetric reflection 400 for samples before the annealing: *a* alloying with boron; *b* alloying with arsenic. *1,2* – without US treatment; *3,4* – with US treatment



a

b

Fig. 4. DRCs for the asymmetric reflection 113 before the annealing: *a* alloying with boron; *b* alloying with arsenic. *1,2* – without US treatment; *3,4* – with US treatment

sample. For the asymmetric reflection 113, we observe some increase of the diffuse scattering in the region of smaller angles, which is caused by the introduction of defects into the Si lattice.

The analysis of DRCs indicates that, in the process of implantation, the concentration of small-size point defects increases (the growth of the intensity of diffuse scattering on "tails" in the region remote from a site of the reciprocal lattice), Figs. 3 and 4. Moreover, for reflection 400 (deeper regions of the crystal), the concentration of point defects of the interstitial type dominates in the crystal implanted with ions of boron under the action of US. The regions positioned near to the surface are more saturated by defects of the vacancy type. This is testified by the analysis of the tails of DRCs for reflection 113.

The presence of diffuse scattering in the regions of great angles, as was shown in [18], is related to the stimulating diffusion of interstitial atoms of Si under the action of US and the accumulation of vacancies in the surface layers of Si. This induces, in its turn, a decrease in the lattice constants in the near-surface region. Thus, the tested regions of a sample for reflection 400 are characterized by the prevalence of compressive stresses caused by interstitial atoms of silicon which diffuse to significant depths under the action of US. Closer to the

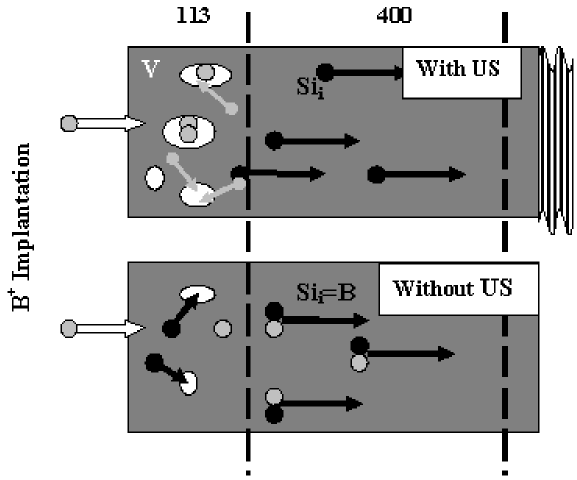


Fig. 5. Model of the formation of defects in near-surface layers of silicon implanted with ions of boron

surface (reflection 113), we observe an insignificant tension of the lattice due to vacancy defects ($\varepsilon = 0.28 \times 10^{-4}$) which is partially compensated by interstitial atoms of implanted boron.

The implantation of ions with different masses (boron, arsenic) under the action of US leads to two different distributions of point defects. On the implantation of boron, interstitial atoms under the action of US diffuse to significant depths, so that their recombination with vacancies is hampered. The implantation of heavier atoms of arsenic leads to the appearance of strongly disordered regions, their overlapping, and the amorphization of the implanted region. In this case, there occurs an insignificant spatial separation of point defects, so that their significant part can recombine on the annealing. In this case, the action of US has no strong effect on the stimulating diffusion of interstitial atoms, because the strongly developed cascade of disorderings has a great number of traps for interstitial defects. The potential relief for the diffusion of interstitial atoms is deeper as compared with that in the case of the implantation of boron, where single interstitial atoms are created along the deceleration track for B ions. Since the covalent radius of As (0.58 nm) is greater than that of Si (0.42 nm), and interstitial atoms are positioned only at small distances from vacancies, we observe the compression of the lattice in this case.

During the annealing of samples, the quasichemical reactions due to the interaction of point defects and impurity atoms are running. Vacancy defects partially recombine with interstitial defects. Implanted atoms of boron and arsenic occupy the positions of sites of the lattice. Since the samples implanted with the US treatment have the greater concentration of vacancies in the surface region due to the separation of point defects, the solubility of boron increases and its precipitation is absent. This is testified by the curves of the distribution of boron over depth for the alloyed samples subjected to the US treatment (Fig. 1). On the supersaturation, the interstitial atoms of Si form dislocation loops of the interstitial type, which leads to the appearance of diffuse scattering in the region of smaller angles relative to the exact position for reflection 400. It is important to note that the diffuse scattering on DRCs for reflection 113 is essentially less for annealed samples implanted with the US treatment, which testifies that a great part of boron is positioned at sites of the lattice. In the samples implanted with boron with the action of US, we observe the increase of sizes of interstitial defects (the Table), which is an additional confirmation of the presence of excessive interstitial atoms of silicon which form dislocation loops of greater sizes on the annealing as compared with those for the sample implanted without US.

A somewhat different situation is observed on the implantation of ions of arsenic. In this case, as mentioned above, no significant separation of point defects occurs. The excessive vacancies promote the fast diffusion of arsenic to the surface of a sample, which is confirmed by the data of mass-spectrometry, Fig. 2. The free vacancies recombine with interstitial atoms that are located in the immediate vicinity of vacancies. A part of vacancies is filled by atoms of arsenic. The excessive atoms of Si form defects of the interstitial type, whose sizes are smaller than those for the samples implanted under the action of US (the Table). The effect of the decrease of the size defects in the samples implanted under the action of US is related to the fast diffusion of arsenic over vacancies to the surface, so that a less part (as compared with that of the control sample) of vacancies in the region of disorderings is filled by atoms of arsenic. The rest of vacancies recombines with interstitial Si. Hence, the concentration of excessive interstitials in the samples implanted without US is greater than that in the samples implanted with the action of US, which leads to the increase in sizes of residual defects after the annealing in the first case.

Thus, the process of action of US can be represented as follows. On the implantation of light atoms (boron), US stimulates the active spatial separation of vacancies and interstitial atoms (Fig. 5). On the subsequent annealing, atoms of boron are captured by vacancies, and excessive interstitial atoms of Si are condensed into clusters.

The implantation of heavy ions (arsenic) leads to the amorphization of the near-surface region, and though the effect of the spatial separation of point defects under the US treatment is observed, but it is essentially less pronounced. The presence of the separation of defects is testified by both a growing accumulation of arsenic near the surface and a decrease in the size of defects after the annealing of the samples implanted under the action of US.

5. Conclusions

The implantation of B^+ into Si samples causes the increase of mechanical stresses in the near-surface regions of plates.

The additional action of US on the implantation leads not only to some decrease of stresses, but also to the change of the sign of a deformation which is induced by the redistribution of point defects and by the variation of their sizes. This is well illustrated by the behavior of the intensity on the tails of DRCs.

The annealing of samples at $T = 800 \div 900$ °C leads to the relaxation of stresses in both the initial samples and in the implanted ones irrespective of the type of ions. Ultrasound stimulates this process of relaxation yet more.

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ОСОБЛИВОСТІ ДЕФЕКТОУТВОРЕННЯ У ПРИПОВЕРХНЕВИХ ШАРАХ МОНОКРИСТАЛІВ КРЕМНІЮ ПРИ АКУСТОСТИМУЛЬОВАНІЙ ІМПЛАНТАЦІЇ ІОНІВ БОРУ ТА МИШ’ЯКУ

О.Й. Гудименко, В.П. Кладько, В.П. Мельник, Я.М. Оліх, В.Г. Попов, Б.Н. Романюк, М.В. Слободян, П.П. Когутюк

Резюме

Вивчено особливості трансформації системи точкових дефектів і пружних деформацій у приповерхневих шарах кремнію, підданих імплантації іонами B^+ і As^+ при одночасній (*in situ*) дії ультразвуку (УЗ). Як метод вивчення структурної досконалості імплантованих структур використано багатокристальну рентгенівську дифрактометрію. Методом мас-спектрометрії вторинних постіонізованих нейтральних частинок досліджено товщинні розподіли імплантованих домішок після термічного відпалу зразків і вплив на них УЗ-обробки. Показано, що імплантація B^+ в зразки Si приводить до збільшення механічних напружень у приповерхневій області пластини. Додаткова дія УЗ при імплантації приводить не лише до деякого зменшення напружень, але й до зміни знака деформації, що викликано перерозподілом точкових дефектів, а також варіаціями їх розмірів. Відпал зразків при $T = 800 \div 950$ °C приводить до релаксації напружень як у вихідних зразках, так і в імплантованих незалежно від типу іонів, а дія УЗ ще більше стимулює цей процес релаксації. Запропоновано фізичну модель виявлених ефектів.