JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 11 No 3, 03010(6pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 11 № 3, 03010(6cc) (2019)

Modification of the Defective Structure of Silicon under the Influence of Radiation

G.P. Gaidar*, M.B. Pinkovska, M.I. Starchyk

Institute for Nuclear Research of the NAS of Ukraine, 47, Nauky Prosp., 03028 Kyiv, Ukraine

(Received 05 March 2019; revised manuscript received 10 June 2019; published online 25 June 2019)

The features of defect formation in the surface and near-surface silicon layers under the influence of irradiation with beams of high-energy ions of gases of various masses are investigated and the prospects of using such ion beams are shown for the technology of radiation doping of semiconductors. It has been established that the degree of Si damage both in the ion path region and in the braking region of ions rises and becomes more complex with an increase in the energy and mass of the ions. The greatest structural damages were observed in the ion braking region, where the concentration of defects was maximal. It was revealed that the structure of the path range after irradiation with protons did not change significantly, in contrast to the heavily damaged structure after irradiation with alpha particles. More orderly and narrower lines of stress associated with defects were observed in Si irradiated with protons, and their number and location relative to the braking line depended on the ion beam intensity. It was established for Si irradiated with alpha particles that the area of their braking consists of the voids with various sizes and shapes etched as a continuous layer and in the form of individual clusters, accompanied by dislocation loops that were formed. It was found that complex structure of the deuteron braking band in Si is due to the presence of dislocations in the initial Si, their movement and interaction with radiation defects at irradiation. The definitive picture of the formation and ordering of defects is determined by the interaction of growth and radiation defects and temperature at irradiation. Changes in the width of the etched braking band in the range from 20 to 200 μm, depending on the mass of ions, are revealed. The minimal width of the braking band for all types of radiation was obtained at the edge of irradiated area, where the sample temperature was lower due to cooling, and the maximal one was obtained in the center of irradiated area.

Keywords: Silicon, Irradiation, Fluence, Ion beams, Defect structure.

DOI: 10.21272/jnep.11(3).03010

PACS number: 61.82.Fk

1. INTRODUCTION

In the modern conditions the modification (the directed change) of the properties of semiconductor materials by the ion beams is one of the most promising physico-technological methods [1, 2]. The electrophysical characteristics of semiconductors can be varied over a wide range, using controlled introduction of radiation defects and performing the necessary heat treatments.

The use of ion implantation as a method of precision local doping of solids provided, in fact, the realization of the advantages of planar technology in microelectronics [3, 4]. The rapid development of microelectronics in recent decades is largely associated with ion implantation [5]. The process of ion doping is associated with minimal degradation of such electrophysical parameters of the initial single crystals as carrier lifetime and conductivity, on which the characteristics of semiconductor devices significantly depend.

It is believed that the ion fluence of 10^{16} cm^{-2} is the threshold fluence to form gas-vacancy complexes in silicon. A more accurate value of the fluence is determined by the temperature of implantation, energy and mass of ions. Nanopores, which are the controllably incorporated into the crystal matrix during the implantation of gas ions, are able to extract undesirable impurities from the volume and serve as centers of stress relaxation in the surrounding lattice [6]. Upon annealing of irradiated silicon at 800 °C, the restore of disintegrated amorphous structure occurs through epitaxial recrystallization on both sides of the amorphous layer [7]. The process begins at the boundary between the amorphous layer and Si matrix. Recrystallization promotes acceleration of the gas segregation, the restoration of the defect structure (amorphous layer) and formation of a polycrystalline layer with stacking faults and dislocations [8]. For this reason, to avoid amorphization step implantation is carried out at elevated temperatures. High-energy ion irradiation provides such defect structuring, i.e., formation of enriched or depleted defect regions by varying the beam current (irradiation intensity). It should be noted that the mechanisms of amorphization and recrystallization under ion irradiation of silicon are still under discussion. Because of the lack of reliable data on the nature and parameters of the altered layers, it is impossible to determine the precise threshold fluence of irradiation, period and size of these superstructures. In addition, in the case of the large ion fluence, the formation of ordered quasi-periodic structures is observed in the irradiated materials [9].

Modern radiation doping of semiconductors with ion beams is characterized by the formation of layers with properties that differ from the matrix properties, due to the controlled introduction of impurities and defects. This method allows to obtain hidden layers with a different type of conductivity, the formation of *p*–*n*-junctions, the passivation of stresses and defects, and the production of new electrical and photovoltaic characteristics.

The irradiation method of semiconductors by intrinsic and impurity ions of keV energies for many years has been the basis of microchip technology. The use of heavy ions with energies of hundreds of MeV has become relevant in connection with the creation of power-

---

* gaydar@kinr.kiev.ua

ful accelerators. At present, the ion energy range within tens of MeV remains the least studied.

The aim of the work was: to reveal the features of the distribution of structural defects in silicon close to the proton braking region and beyond its limits by the methods of X-ray topography and selective etching; to establish the modification peculiarities of defect structure in the near-surface silicon layers when irradiated with ions of gases of various masses with energies of tens of MeV; and also to summarize the obtained experimental results.

2. RESEARCH METHODS

The structural properties of irradiated silicon samples were studied using a number of techniques such as X-ray topography, selective etching, metallography.

- X-ray topography is a non-destructive method for studying the structural defects in crystals, based on the interaction of incident X-rays with a crystal lattice. X-ray diffraction and absorption are affected by various lattice defects. This method allows obtaining the information about point defects, dislocations, stacking faults, grain boundaries, precipitates (particles of a new phase), pores, and their distribution in the crystal bulk [10].
- Selective etching is based on the chemical etching of silicon and fixes the difference in oxidation in the defective and defect-free regions of the crystal. The chemical etching is an important procedure when working with silicon. The action of chemical etchant includes polishing effect and selective etching. In the experiments, the etchant of such composition $2HNO_3 + HF + CH_3COOH$ was used. The first component (nitric acid) oxidizes the sample surface, the second (hydrofluoric acid) makes it soluble, and the third component (acetic acid) serves as a buffer that controls the reaction rate.

When etching the defect-free surface of the semiconductor, it remains plane and clean. Areas with defects are etched differently, forming "pits" or "knobs". The stacking faults, some "inclusions", small dislocation loops are etched in the form of flat pits. Dislocations are etched in the form of dimples with top, which deepen with an increase in the duration of etching without changing their shape and morphology. If the dislocation is not perpendicular to the surface, the shape of the dimple will be incorrect. In general, at the beginning of etching, the linear and localized defects may have the same morphology, but with an increase in the duration of etching, the former remains of their shape and the localized defects manifest their flat bottom. Some defects of the crystal appear during etching as "knobs". This, as a rule, may be small insoluble oxidized particles or a precipitate that falls out from the etchant.

The result of etching the sample surface depends on its crystallographic orientation. The densely packed planes are usually easier to etch. For single silicon crystal, these are the (111) and (110) types of planes. The shape of etching patterns is also determined by the type of crystallographic plane. Etching pits associated with dislocations, when re-etching the crystal, appear in the same places as previously found. In this way the dislocations that intersect the sample surface are detected. The dislocation loops that intersect the sample surface appear as two coupled etch pits.

- Metallography makes it possible to detect the inner structure of defects (porosity, inclusion of different phases, structural defects) and analyze the structure of the surface layer.

3. EXPERIMENT

Single crystals of n-Si ($\rho = 3\text{-}4$ kOhm·cm) grown by the Czochralski method, dislocation-free and with a dislocation density of $\sim 10^3\ \text{cm}^{-2}$ are investigated. Irradiation of silicon crystals by protons (H^+) with an energy of 6.8 MeV, by 13.6 MeV deuterons ($^2H^+$) and 27.2 MeV alpha particles (He^{2+}) by fluences $\Phi \geq 10^{16}\ \text{cm}^{-2}$ with varying the ion beam current density from 0.25 to 3 μA/cm^2 was carried out at cyclotrons U-120 of the Institute for Nuclear Research of the NAS of Ukraine. The dislocation-free crystals were irradiated with protons and alpha particles, and crystals containing dislocations were irradiated with deuterons. Samples were cooled with running water during irradiation. Meanwhile the temperature of the samples did not exceed 100 °C. To study the topographic image of the defective silicon microstructure, the irradiated samples were cut along the direction of irradiation into plates (which made it possible to study the properties of silicon in the ion path region, braking and behind the braking area), the mechanical (grinding) and chemical (polishing) surface treatments were carried out. To study the layer-by-layer distribution of structural defects in silicon irradiated with protons, the samples were thinned by gradual etching (with the step of 30 μm) from the side of the irradiated surface. In silicon, the projection (calculated) path length of protons and alpha particles of utilized energies is approximately the same and is about $R_p \approx 360$ μm, and in the case of deuterons it is 780 μm.

4. RESULTS AND DISCUSSION

As a result of the carried out researches the number of features of the behavior of radiation defects under conditions of their high concentration and non-uniform distribution were elucidated. According to the data of X-ray topography and selective etching, it was found that the greatest structural damages (disordering) for all types of radiation were observed in the braking region of ions, where the concentration of defects was maximal (bands 1 in Fig. 1). The dependence of the damage degree of the defect silicon structure on the mass of the irradiating particles was established: the structure of the path range after irradiation with protons did not change significantly (Fig. 1a), in contrast to the heavily damaged structure (possibly, polycrystalline) after irradiation with alpha particles (Fig. 1c). More ordered stress lines associated with defects were observed in silicon irradiated with protons.

The significant changes in the width of the etched braking band for light ions of different masses were found in the direction from the edge to the center of the irradiation region: 30-90 μm (for H^+), 20-130 μm (for $^2H^+$), 140-200 μm (for He^{2+}). The minimal bandwidth for all types of irradiation was obtained at the edge of the irradiation area, where the sample temperature was lower due to cooling.

In the center of the irradiation region of the sample at the beam current density of protons ≤ 0.45 μA/cm^2 at the distance from the surface, equal to double path length of the ions ($2\,R_p$), the second etched line of stress was observed parallel to the braking line 1 (long-range effect) (Fig. 1a, line 2). The dependence of the propagation of defects behind the braking line of hydrogen ions on the value of the ion beam current density, that is, on the intensity of irradiation, is revealed. When the current density increased to 1 μA/cm^2, the stress line 2 in Si was not observed behind the braking line 1.

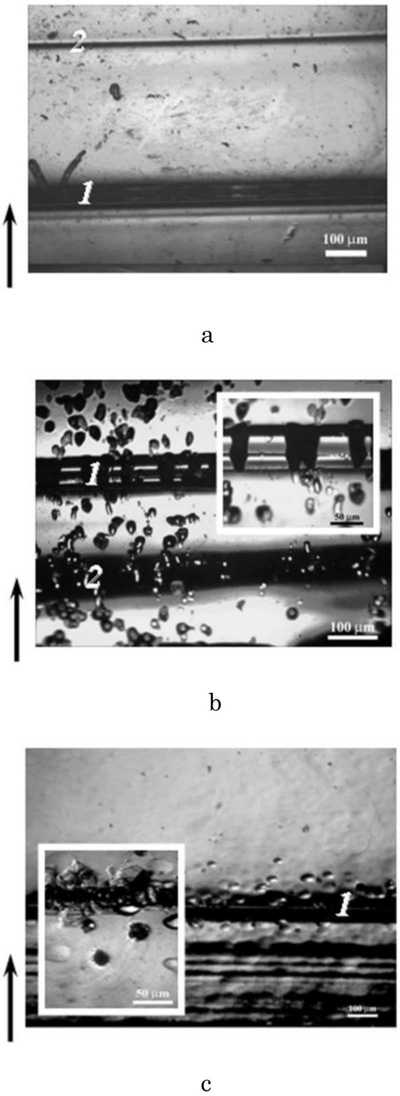

Fig. 1 – Micrographs of selective etching (in the center of the irradiation region) after irradiation of *n*-Si with: a – protons; b – deuterons; c – alpha particles. The fluence of irradiation is 10^{17} cm^{-2}. The arrows show the direction of irradiation; 1 is the ion braking region; 2(a) is the stress line associated with defects beyond the braking area of H$^+$ at the distance of the double ion path (about 720 μm) (long-range effect); 2(b) is the stress band associated with defects within path region of ^{2}H$^+$ at a distance of about 130 μm from the braking band 1. The insets show segments of the braking bands 1 of ions in expanded scale

At the beam current density 3 μA/cm^2 under similar cooling conditions (the sample was cooled only with running water), the part of silicon, whose thickness corresponded to the path depth of ~ 360 μm, at the passage of ions was peeled off from the main crystal volume during irradiation (Fig. 2). This fact indicated that the temperature of silicon in the braking region reached a value sufficient to release hydrogen from Si-H bonds and to fill the vacancy complexes in the process of irradiation. According to [11], hydrogen released from Si-H bonds at the temperature near 600 °C formed bubbles that grew and burst to create the voids (pores), sizes and density of which were determined by the energy of protons and the irradiation intensity. At low beam current density of 0.25-0.45 μA/cm^2, the irradiated part of silicon peeled off only after the annealing of irradiated silicon at 600 °C, that is, the effect was determined by the sample annealing temperature.

Fig. 2 – Photographs of the Si surface (in different perspectives) irradiated with 6.8 MeV protons by fluence of $3\cdot10^{17}$ cm^{-2} at the beam current density of 3 μA/cm^2. The irradiation of silicon at the elevated temperatures leads to the separation of the irradiated part of the sample due to high stresses in the ion braking region when the breaking of Si-H bonds occurs with the release of hydrogen

The distributions of the structural defects near the braking area of protons in silicon were obtained by X-ray topography and selective etching methods after the gradual etching of the surface of irradiated silicon (from the irradiation side) with the step of 30 μm. Silicon samples were pre-irradiated at $T \leq 100$ °C with proton fluence of 10^{17} cm^{-2} and annealed for 0.5 h at a temperature of 580 °C. Namely under these conditions hydrogen begins to be released from the Si-H bonds. The results obtained help to understand the behavior of hydrogen in silicon, when the temperature of the sample during irradiation is quite high.

Fig. 3 and Fig. 4 show respectively the pictures of X-ray topography and selective etching of the sample taken in the irradiation plane at a depth of 315-510 μm from the irradiated surface. Taking into account that the projection length of free path of protons with the energy of 6.8 MeV is about 360 μm, the data are obtained for 45 μm (a) and 10 μm (b) to the braking line, as well as for 35 μm (c) and 150 μm (d) behind it. It can be seen that the irradiated area associated with radiation defects gradually decreases under deepening into the material and disappears completely at the depth of about 510 μm from the irradiated surface (nearly 150 μm behind the braking line). The layers of growth of the matrix silicon were detected at the depth of about 395 μm (Fig. 3c), that is, almost 35 μm behind the proton braking line. In our opinion, these growth layers were decorated with hydrogen in the presence of oxygen, carbon and other growth impurities and defects. Such layers were not detected with further etching at the depth of more than 150 μm behind the braking line of the protons (Fig. 3d).

That is, in silicon, irradiated with 6.8 MeV protons and annealed at 580 °C, the contrast associated with growth layers appears in a narrow line behind the braking part and does not further appear.

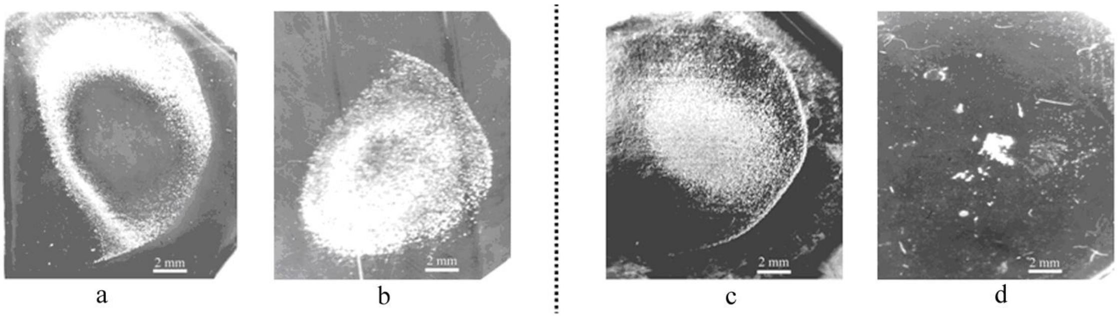

Fig. 3 – X-ray topograms of the structure of irradiated silicon ($E_{H+} = 6.8$ MeV; $\Phi = 10^{17}$ cm^{-2}) after annealing ($T = 580$ °C; $t = 0.5$ h) in the plane of irradiation after gradual etching at the different depths from the irradiation surface: before the braking line (a – 45 μm; b – 10 μm) and behind it (c – 35 μm; d – 150 μm). The vertical dashed line is the proton braking line

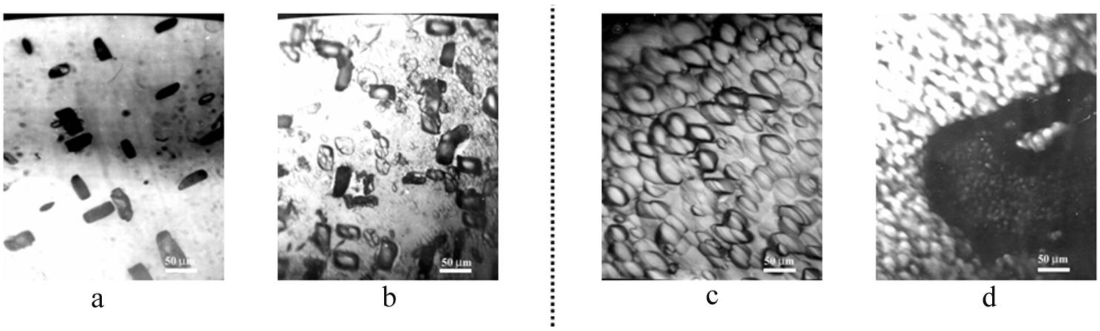

Fig. 4 – Micrographs of the surface structure of irradiated Si after selective etching at appropriate depths. Notations as in Fig. 3

For comparison, in Si irradiated with 43 MeV protons at $\Phi = 10^{17}$ cm^{-2} and annealed for 0.5 h at 800 °C, in the braking region of protons the gradual removal of stresses by plastic deformation with formation of dislocations along the braking line was observed [12]. After annealing at 1000 °C, the contrast of the stresses, which associated with the growth layers of the initial Si, was revealed; it appeared for the protons of this energy earlier behind the braking area, than in path region.

The results obtained for protons of different energies indicate that the features of the Si structure should be determined not only by the temperature of irradiation or annealing, but also by its distribution over the sample during the irradiation process, since it can affect the defective structure in all areas (ion path, braking, behind the braking region).

Micrographs of the structure of irradiated Si after selective etching (Fig. 4), which fix changes in the structure near the braking line of protons at the corresponding depths have shown that the proton path region remains crystalline with detected typical defects (a, b), and behind the braking line the structure of silicon changes (c, d).

Unlike the proton irradiation, in the case of deuteron irradiation of dislocation Si, no long-range effect was observed, however, the braking region of deuterons was not only wider, but also had a more complex structure (Fig. 1b). In the ion path region in Si, the additional etched band of stresses 2 appeared near the center of the irradiated area (at the distance of 130 μm from the first band and closer to the irradiated surface), where the T of the sample during irradiation was maximal. The width of this band was about 100 μm.

During proton irradiation of silicon, the braking region is a rather narrow band (Fig. 1a), with alpha irradiation it consists of pores (Fig. 1c, inset), whereas during irradiation with deuterons the braking region consists of a wide band of damages, located in parallel of the braking plane, and of "bridges" from the defects, probably stacking faults, which crossed the damaged region at right angle (Fig. 1b, inset). Such complex structure is obviously due to the presence of dislocations in the initial Si, their movement, interaction with radiation defects during irradiation (in conditions of high temperature and high concentrations of defects).

The structure of Si on the surface, in the path and braking regions of alpha particles was the most damaged (if compared with the irradiation of protons and deuterons), which could be expected since the energy and mass of H^{2+} were higher.

The structure of the path after irradiation of silicon with protons did not change significantly, in contrast to the heavily damaged structure after irradiation with alpha particles. As in the case of protons, the long-range effect was observed (propagation of defects in the form of stress lines behind the braking line) for alpha particles [12]. This effect depended on the ion beam current density (intensity of irradiation), and occurred only at ions' current density less than ≤ 0.45 μA/cm^2, that is at lower irradiation temperatures.

When the beam current density was increased to 1 μA/cm^2, ordered linear structures were observed only in the path of alpha particles. The number of such structures depended on the intensity of the ion beam (increased with increasing intensity) and, hence, on the heating temperature of the sample during irradiation.

The results of metallographic study for the Si sample irradiated with fluence of 10^{17} cm^{-2} at the ion beam current density close to 1 μA/cm^2 after the selective etching show that the braking region of helium ions was a strongly damaged region of silicon consisting of the voids with various sizes and shapes, etched as a continuous layer and in the form of individual clusters, accompanied by dislocation loops that were formed (Fig. 1c).

The formation of voids during the implantation of high-energy gas ions is most likely due to the high concentration of defects of the vacancy type [13, 14]. The vacancies, merging into the complexes, can remove stresses in the lattice, including those associated with the precipitation of growth impurities (oxygen or carbon), and prevent the formation of dislocations.

Thus, the use of gas ions of MeV energies promotes, on the one hand, to create in the ion braking region of silicon a broken layer, and on the other hand, it can contribute to the accelerated recrystallization of amorphous layers due to the temperature increase during irradiation as a result of an increase in the ion energy. This contributes to the layerwise segregation of impurities and defects in Si, that is, the change in properties both in the ion path and behind it. To obtain the specific values of these changes, it is important to control the regime of irradiation (type of ions, their energy, fluence and temperature of irradiation).

5. CONCLUSIONS

1. The results of studies of modification of the silicon defect structure under the influence of radiation showed that collective interaction processes under conditions of high density of atomic collisions could stimulate inner phase transformations, causing the formation of layers of defects and changing the matrix parameters.
2. It was revealed that the number and width of etched stress lines (the nature of defect formation) when silicon is irradiated with large fluences of ions depends on their mass and energy. This makes it possible in the depth of silicon (≤ 780 μm) to create thin layers of different widths (20-200 μm), the properties of which differ from those of the original matrix.
3. The ability to change the properties of silicon layer by layer is important for the development of radiation doping of semiconductors and to ensure the current needs of micro- and nanoelectronics.
4. Understanding the processes of orderly accumulation and distribution of defects and impurities during ion irradiation is necessary to control their quantity and localization.

ACKNOWLEDGEMENTS

The authors are grateful to Sugakov V.I., the Corresponding Member of the NAS of Ukraine, for fruitful discussion and valuable comments.

REFERENCES

1. K.K. Kadyrzhanov, F.F. Komarov, A.D. Pogrebnyak, V.S. Rusakov, T.E. Turkebaev, *Ion-Beam and Ion-Plasma Modification of Materials* (Moscow: Izdatelstvo Moskovskogo Universiteta: 2005) [in Russian].
2. V.A. Kozlov, V.V. Kozlovski, *Semiconductors* **35** No 7, 735 (2001).
3. N. Teranishi, G. Fuse, M. Sugitani, *Sensors (Basel)* **18** No7, 2358 (2018).
4. A.L. Stepanov, V.I. Nuzhdin, V.F. Valeev, V.V. Vorobev, T.S. Kavetskyy, Y.N. Osin, *Rev. Adv. Mater. Sci.* **40**, 155 (2015).
5. L.A. Larson, J.M. Williams, M.I. Current, *Rev. Accel. Sci. Technol.* **04** No 01, 11 (2011).
6. R. Kögler, A. Peeva, P. Werner, W. Skorupa, U. Gösele, *Nucl. Instrum. Methods Phys. Res. B* **175-177**, 340 (2001).
7. J. Nord, K. Nordlund, J. Keinonen, *Phys. Rev. B* **65** No 16, 165329 (2002).
8. V.M. Vishnyakov, S.E. Donnelly, G. Carter, *J. Appl. Phys.* **94** No 1, 238 (2003).
9. V.I. Dubinko, A.G. Guglya, S.E. Donnelly, *Nucl. Instrum. Methods Phys. Res. B* **269** No 14, 1634 (2011).
10. P.I. Baranskii, O.Ye. Bieliaiev, G.P. Gaidar, V.P. Kladko, A.V. Kuchuk, *Problems of Diagnostics of the Real Semiconductor Crystals* (Kyiv: Naukova dumka: 2014) [in Ukrainian].
11. A.A. Groza, P.G. Litovchenko, M.I. Starchyk, *Radiation Effects in Infrared Absorption and Silicon Structure* (Kyiv: Naukova dumka: 2006) [in Ukrainian].
12. A.A. Groza, P.G. Litovchenko, M.I. Starchik, V.I. Khivrich, G.G. Shmatko, *Ukr. J. Phys.* **55** No 6, 699 (2010).
13. A. Peeva, R. Kögler, W. Skorupa, J.S. Christensen, A.Yu. Kuznetsov, *J. Appl. Phys.* **95**, 4738 (2004).
14. J.S. Williams, M. Conway, B.C. Williams, J. Wong-Leung, *Appl. Phys. Lett.* **78**, 2867 (2001).

Модифікація дефектної структури кремнію під впливом радіації

Г.П. Гайдар, М.Б. Пінковська, М.І. Старчик

Інститут ядерних досліджень НАН України, пр. Науки, 47, 03028 Київ, Україна

Досліджено особливості дефектоутворення у поверхневих і приповерхневих шарах Si під впливом опромінення пучками високоенергетичних іонів газів різних мас і показано перспективи використання таких іонних пучків для технології радіаційного легування напівпровідників. Встановлено, що ступінь пошкодження Si як в області пробігу іонів, так і в області їхнього гальмування збільшується і ускладнюється зі збільшенням енергії і маси іонів. Найбільші порушення структури спостерігалися в області гальмування іонів, де концентрація дефектів була максимальною. Виявлено, що структура області пробігу після опромінення протонами істотно не змінювалася, на відміну від сильно пошкодженої структури після опромінення альфа-частинками. Більш впорядковані та вузькі лінії напружень, пов'язані з дефектами, спостерігалися в Si, опроміненому протонами, а їхня кількість і розташування щодо гальмівної лінії залежали від інтенсивності пучка іонів. Встановлено для Si, опроміненого альфа-частинками, що область їхнього гальмування складається з порожнеч різних розмірів і форм, витравлених як суцільний шар та у вигляді окремих кластерів, що супроводжуються дислокаційними петлями, які утворилися. З'ясовано, що складна структура смуги гальмування дейтронів у кремнії зумовлена наявністю дислокацій у вихідному Si, їхнім рухом і взаємодією з радіаційними дефектами при опроміненні. Остаточна картина формування і впорядкування дефектів визначається взаємодією ростових і радіаційних дефектів і температури при опроміненні. Виявлено зміни ширини витравленої смуги гальмування в межах від 20 до 200 мкм залежно від маси іонів. Мінімальну ширину гальмівної смуги для всіх типів опромінення отримано на краю опромінюваної області, де температура зразка була нижчою внаслідок охолодження, а максимальну – в центрі опромінюваної області.

Ключові слова: Кремній, Опромінення, Флюенс, Іонні пучки, Дефектна структура.