ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 4, № 3 (2003) С. 470-473

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 4, № 3 (2003) P. 470-473

УДК 541.183.5, 539.219.3

ISSN 1729-4428

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Nitrogen as Annihilation Centre for Point Defects in Implanted Silicon

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The accumulation of radiation defects in silicon implanted with 150 keV N^+ ions at high ion current density (20 μA cm^{-2}) and low density (0.05 μA cm^{-2}) was investigated by means of X-ray double-crystal spectrometer and EPR method. At high ion current density the radiation defects accumulate up to amorphization at the ion dose of 1×10^{15} cm^{-2}. At low ion current density the curve of lattice parameter change on dose has oscillatory view and amorphization of the layer is not achieved at least up to ion dose of 1.4×10^{16} cm^{-2}. The processes of the nitrogen atoms capture on the vacancy defects and Watkins displacement of them from the nodes work as additional channel of radiation defect annihilation. At high ion current densities and at high level of ionization in the implanted layer process of Watkins substitution is suppressed.

Keywords: silicon, ion implantation, radiation defects, defect annihilation, nitrogen.

Стаття поступила до редакції 19.05.2003; прийнята до друку 23.08.2003.

I. Introduction

The investigations of radiation defects accumulation in silicon during implantation at various ion current densities provide opposite results. On the one hand, strong dependence of the efficiency of stable defects production is known at B^+ ion implantation [1]. On the other hand, for P^+ or Si^+ ions this dependence is slight [2] or is absent [3]. It was supposed that the dependence of production rate of the stable defects versus ion current density was conditioned by interaction of newly created mobile vacancies and self-interstitials with the earlier introduced point defects. It was believed that the stable defects were not primary but were formed in result of simple defect corporation. But it is determined that self-interstitial defects in silicon (Si-P6 [4], Si-B3 [5], Si-A5 [6], Si-O2 [7]) are the primary defects. According to analysis [8] general vacancy defects – divacancies are the primary defects too and not only at irradiation with light particles (gamma rays, electrons) but at irradiation with fast neutrons and ions.

In this work we investigate the radiation defects accumulation in silicon implanted with N^+ ions at various ion current densities.

II. Experimental details

The accumulation of radiation defects was determined from the change of the crystal lattice period Δa of the silicon layer. The Δa values were measured from the angle difference between diffraction maxima of the X-ray reflection from the implanted layer and the substrate. The diffraction curves were measured by a double crystal X-ray spectrometer for a parallel position of the crystal-monochromator with the sample using $CuK\alpha_1$ irradiation in the fourth order of a (111) reflection. The accuracy of the determination of the Δa was ± 1×10^{-5} Å. The concentration of the radiation defects was estimated from the Δa values taking into account the values of the atom displacement in the regions of prevalent defects which is equal to 0.2 Å [9].

The beginning of the amorphization process was detected by the EPR method by the appearance of the isotropic line with a g-factor of 2.0055.

Sheet charge carrier concentration in the implanted layers was obtained from the Hall effect and electrical conductivity measurements using the Van der Pauw configuration [10].

Isochronal (15 min) annealing of the samples implanted with ions was carried out in a vacuum chamber with and without simultaneous 10 keV electron illumination with a current density of 5 mkA cm^{-2}. The accuracy of temperature during annealing was ± 2 ^{o}C.

III. Experimental results and discussion

In fig. 1 changes of the lattice period Δa versus the N^+ ion dose Φ (Δa(Φ)) are compared for high (20 μA cm^{-2}, scanning beam – J_{ef} =0.5 μA cm^{-2}) ion current density (curve 1) and low (0.05 μA cm^{-2}) density (curve 2). At

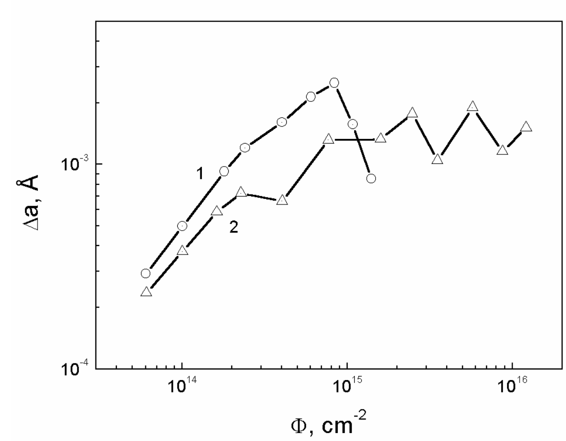

Fig. 1. Dependence of the lattice period of Si crystals on N^+ ion dose. Ion current density: 1) – 20 μA cm^{-2}; 2) – 0.05 μA cm^{-2}.

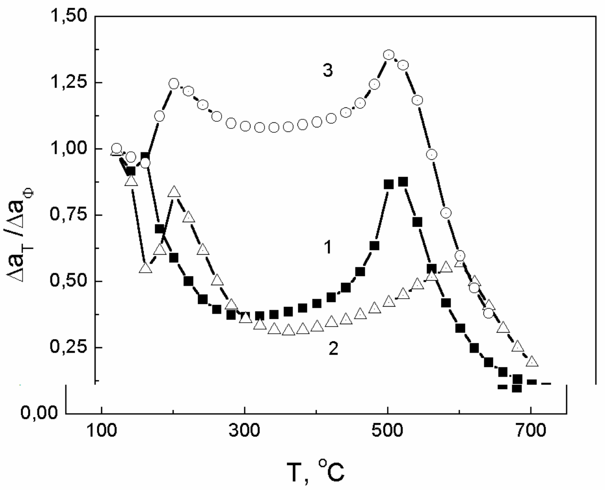

Fig. 2. Lattice period reconstruction at isochronal annealing of the heavily B-doped and implanted silicon. 1) – Si^+, 1×10^{14} cm^{-2}; 2) – P^+, 1×10^{14} cm^{-2}; 3) – N^+, 3×10^{14} cm^{-2}

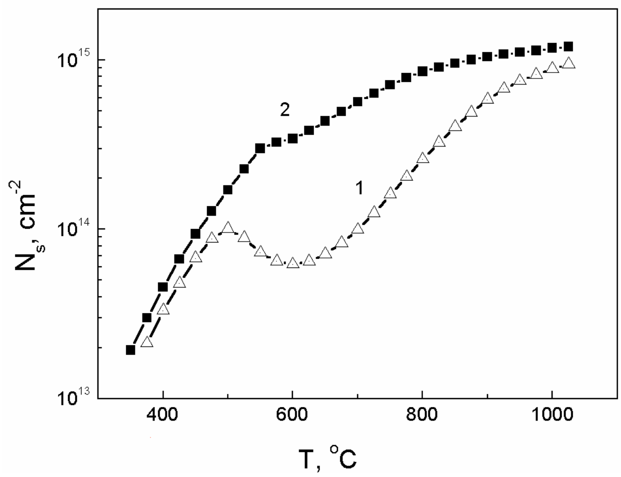

Fig. 3. Curves of electrical activation of ion-implanted boron in silicon. 1) – B^+, 1.3×10^{15} cm^{-2}; 2) – B^+, 1.3×10^{15} cm^{-2}, annealing with electron illumination.

high ion current density the linear character of radiation defects accumulation takes place up to ion dose of 2×10^{14} cm^{-2}. At the higher doses the curve of lattice period change has sublinear character ($\Delta a(\Phi) \sim \Phi^{0.5}$). The change of the lattice period Δa reaches its maximum at a dose of 9×10^{14} cm^{-2} and then a bend is observed at the higher doses. At these doses the diffraction curves from the implanted layer become broader and their intensity is reduced. Simultaneously a line with g-factor 2.0055 is detected in EPR spectra; this is typical for amorphous silicon.

At low ion current density the curve $\Delta a(\Phi)$ has oscillatory view at doses higher then 4×10^{14} cm^{-2}. In this case amorphization of the layer is not achieved at least up to ion dose of 1.4×10^{16} cm^{-2}.

In fig. 2 the curves of isochronal annealing of the silicon high doped with boron (ρ = 0.005 Ohm cm) and implanted with Si^+ (curve 1), P^+ (curve 2), or N^+ (curve 3) ions are shown. For heavily B-doped and implanted silicon, curves of lattice period reconstruction have two regions of inverse annealing.

Fig. 3 shows the electrical activation curves of the impurity in silicon implanted with boron at a dose of 1.3×10^{15} cm^{-2} (curve 1). The activation of boron during thermal treatment with simultaneous electron illumination is shown by curve 2. As it is seen, the illumination reduces the stage of "reverse annealing" in the isochronal annealing curves of boron-implanted silicon.

Fig. 4 shows schematically the motion of interstitial Si atom under elastic deformation field caused by impurity atom in the lattice node.

The oscillations of the curve $\Delta a(\Phi)$ presented in Fig. 1 are the result of interaction of nitrogen atoms with the point defects (vacancy type and self-interstitials). In equilibrium conditions nitrogen is feebly dissolved in silicon. However, nitrogen atoms are trapped on vacancy defects, i.e. in the lattice nodes at the high concentrations of point defects (at ion dose of 4×10^{14} cm^{-2} concentration of radiation defects in the layer is $(3\text{-}4)\times10^{19}$ cm^{-3}). As tetrahedral covalent radius of N atom (0.7 Å) is less than radius of Si atom (1.175 Å) the lattice period of silicon decreases. The estimations have shown that the concentration of nitrogen atoms in the nodes is 6×10^{18} cm^{-3} at the dose of N^+ ions 4×10^{14} cm^{-2}. In this case the complete nitrogen concentration in the layer is 1×10^{19} cm^{-3}. At dose of 4×10^{15} cm^{-2} these values are 1×10^{20} and 3×10^{19} cm^{-3}, accordingly.

Nitrogen atoms in the nodes are the deep donors in silicon crystals [11]. They may change the charge states of the radiation defects. Annealing temperatures of the radiation defects depend on their charge states. It can be used for evidence that implanted N may be localized in the lattice nodes. In [12,13] concentrations and annealing temperatures of interstitial complexes were determined by X-ray diffraction method. These studies used the well-known phenomenon of self-interstitial atom substitution for group III elements in the lattice nodes of silicon (Watkins substitution [14]). This substitution effect takes place not only upon irradiation, as observed by Watkins,

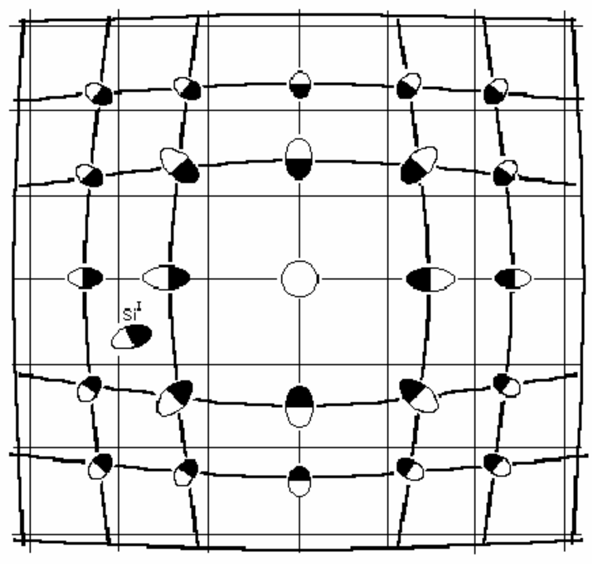

Fig. 4. Motion of interstitial Si atom under elastic deformation field.

but also in the process of thermal treatment of the implanted samples at the temperatures of interstitial defect annealing. The displacement process of boron atoms from the lattice nodes can be controlled by the experimentally observed change in the crystal lattice constant. The covalent radius of B atoms is smaller (0.8 Å) than of Si atoms (1.175 Å) and these atoms, being positioned at the nodes, compress the silicon lattice. The lattice constant is growing as the boron atoms are displaced from the nodes. In silicon heavily doped with boron (ρ = 0.005 Om cm) the stages of "inverse annealing" are superimposed on the curves of the lattice constant recovery (fig. 2). The interstitial complexes are annealed at 120 and 480°C (curve 1) in the case of Si^+ ions, while in the case of P^+ ions the annealing temperatures are 160 and 560°C (curve 2). The differences in annealing temperatures of interstitial defects were associated with their charge states [12,13]. The defects in the heavily boron-doped silicon implanted with Si^+ ions are in a positive charge state. It is well known that a considerable portion (up to 70%) of the implanted impurity B or P is located in the lattice nodes during implantation [15]. Because of this, upon implantation of the P^+ ions into silicon heavily doped with boron compensation of charges takes place and the interstitial defects are in a neutral charge state (annealing stages 160 and 560°C).

In the case of N^+ ion implantation (curve 3) the first stage (160°C) corresponds to anneal of the interstitial defects in neutral charge state. It is the evidence that implanted N atoms localize mainly in the lattice nodes. On the second stage (480°C) interstitial defects anneal in a positive charge state, because at 430°C nitrogen atoms leave the nodes and don't return in the nodes again [11].

At the subsequent irradiation th N atoms are displaced from the lattice nodes by interstitial Si atoms (Watkins substitution). Watkins observed the substitution effect in silicon doped with B, Al, Ga [14]. In the work [16] authors concluded that substitution effect takes place for all impurities with covalent radii different from the radius of the lattice atom. The elastic strains created by the impurity atoms in the nodes are the cause of the direct movement of the self-interstitials in the lattice toward dilatation (compression) centers with subsequent displacement of the impurity atoms from the nodes. It is not difficult to consider this movement at a microscopic level. The lattice atoms displaced from the equilibrium positions in the first coordinate sphere relative to the impurity atom and to less extent in the subsequent spheres (fading) are polarised and generate an electric dipole moment. Under the influence of the dipoles of the displaced atoms the interstitial Si atoms obtain inductive dipole moments. Since the magnitude of the dipole moment sharply increases towards the center of the deformation the interstitial atom moves to a dilatation (compression) center. This is schematically presented in fig. 4.

At the subsequent irradiation and increase of the radiation defects concentration, the nitrogen atoms are trapped on vacancy defects again and so on. The two processes determine oscillatory character of the curve Δa(Φ). The processes of the nitrogen atoms capture on the vacancies and displacement them from the nodes work as additional channel of radiation defects annihilation. These results allow to explain earlier known fact of point defect clusters formation suppression in silicon ingots doped with nitrogen during growing [17].

But what is the reason that this annihilation process does not work at the high ion current density (fig. 1, curve 1)? We believe that at high ion current density and high level of ionization, nonequilibrium electrons and holes screen dipoles around impurity atoms. As result, Watkins substitution process is suppressed.

We think that any impurity atom in the lattice node with covalent radius different from the radius of lattice atom is the such additional center of defect annihilation, including B atom. The known dependence of stable defects production efficiency on B ion current density may be connected with this annihilation mechanism. In the case of boron it is easy to verify influence of the ionization level on displacement process from the nodes by self-interstitials. The substitution effect is displayed in the curves of electrical activation of implanted boron in the process of thermal treatment at the temperature of interstitial defect annealing (fig. 3). It can be seen from fig. 3 that boron activation curve contains a stage of "reverse annealing" that is caused by the displacement of boron from the lattice nodes with interstitial Si atoms generated during the anneal of interstitial complexes [18]. The electron illumination reduces the efficiency of the displacement process (curve 2).

In the case of Si^+ ion implantation this additional channel of defect annihilation does not work and defect accumulation dependence on ion current density is absent. In the case of P^+ ion implantation this dependence is slight because section of P atom displacement from the nodes is small [16].

IV. Conclusion

The accumulation of radiation defects in silicon implanted with N^+ ions depends on ion current density. This dependence is conditioned by additional channel of defect annihilation via nitrogen atoms capture on the vacancy defects and subsequent Watkins displacement of them from the nodes. Efficiency of the Watkins substitution process is depended on the level of ionization in the implanted layer.

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Азот як центр анігіляції точкових дефектів в імплантованому кремнії

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За допомогою двокристального Х-променевого спектрометра та методу ЕПР досліджено накопичення радіаційних дефектів у кремнії, імплантованому іонами N+ з енергією 150 кеВ при високій (20 мА $см^{-2}$) та низькій (0,05 мА $см^{-2}$) густині струму іонів. При високій густині струму іонів радіаційні дефекти накопичуються аж до аморфизації при дозі до $1*10^{15}$ $см^{-2}$. При низькій густині струму іонів крива зміни параметра гратки має перемінний характер і аморфизація шару не досягається аж до дози іонів $1,4*10^{16}$ $см^{-2}$. Процеси захоплення атомів азоту вакансіями та їх зміщення Уоткінса розглядаються як додатковий канал анігіляції радіаційних дефектів. При високій густині струму іонів і при високорівневій іонізації в імплантованому шарі зміщення Уоткінса подавлюється.