American Journal of Applied Sciences 2 (1): xx-xx, 2005
ISSN 1546-9239

Displacement of Boron from the Silicon Crystal Nodes by Interstitial Si Atoms During Implantation and Annealing

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Abstract: The process of boron displacement from the nodes into interstitial positions by interstitial Si atoms in silicon (Watkins effect) on the conditions of implantation and annealing has been investigated with help of X-ray diffraction and electrical methods. It was revealed that the efficiency of the Watkins substitution is determined by the ion current density (level of ionization). With increasing of the ionization level in the implanted layer during implantation or annealing (additional low-energy electron irradiation) the replacement process may be suppressed.

Key words: Silicon, Ion Implantation, Radiation Defects, Watkins Substitution

INTRODUCTION

Radiation defects are generated in silicon during ion implantation. In the process of subsequent thermal treatment to anneal the defects and activate the inserted impurities, residual extended damages (rod-like defects, stacking faults bounded by dislocation loops) may be formed. These extended damages have interstitial nature. The presence of such impurities as C or B in the silicon crystals (layers) suppresses the formation of residual damages [1-3]. The necessary condition for a positive result is the incorporation of these impurities in the lattice nodes. But it is known that during implantation the quantity of generated interstitial Si atoms exceeds the value for stable interstitial complexes by a factor of roughly 20. The self-interstitials may displace these impurities from the lattice nodes (Watkins substitution effect [4]). Therefore it is needed to preserve these impurities in the lattice nodes during implantation, so that they can later operate as traps for self-interstitials during the heat treatment. In the case of boron it is important for multiple step implantation [5], for example. Using of boron atoms as the traps for self-interstitials must decrease amount of the operations in the multiple step method of ion doping. In this work we investigate the process of boron displacement from the nodes into interstitial positions by interstitial Si atoms on the conditions of implantation and annealing.

MATERIALS AND METHODS

In this work the change of the crystal lattice period Δa was investigated in implanted silicon layers. 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 $CuK_{\alpha1}$ irradiation in the fourth order of a (111) reflection. The accuracy of the Δa determination was $\pm1\times10^{-6}$ nm. Silicon crystals lightly doped with phosphorus (ρ_0 = 0.5 Ω cm) and highly doped with boron (ρ_0 = 0.005 Ω cm) were implanted with a scanning beam of 100 keV B^+ ions with the effective current densities j_{ef}=0.05-0.5 μA cm^{-2}.

The charge carrier concentration was determined from the Hall effect measurements in the Van der Pauw configuration [6].

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

RESULTS AND DISCUSSION

In Fig. 1 the change (growth) of the lattice constant Δa versus the B^+ ion fluence Φ is given for silicon samples lightly phosphorus doped (curve 1) and heavily doped with boron (curves 2, 3, 4), respectively. Curves Δa(Φ) are noticeably higher for silicon heavily doped with boron (ρ_0 = 0.005 Ω cm) than those for the n-type silicon samples. It should be noted that the values of Δa(Φ) are higher for a lower ion current density.

Figure 2 demonstrates the recovery of the lattice constant in silicon layers implanted with B^+ ions during isochronal annealing. In n-type silicon (ρ_o = 0.5 Ω cm) on the first stage (100-280°C) the divacancies are annealed mainly [7]. At the second stage (380-600°C) the multivacancy complexes , e. g. five-vacancy (Si-P1 centres) and others, which remained unidentified [8] are annealed. The same two stages were revealed for silicon implanted with S^+ ions [9].

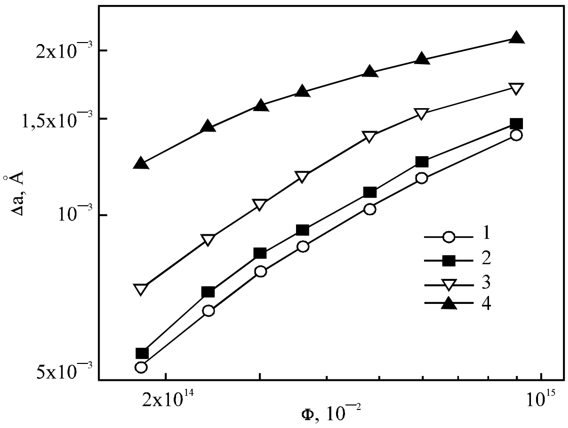

Fig. 1: Dependence of the Silicon Lattice Constant Δa on B^+ Ion Fluence Φ in:-Si:P, ρ_0 = 0.5 Ω cm; (2-4)-Si:B, ρ_0 = 0.005 Ω cm; j_{ef} : (1,3)-0.2; (2) - 0.5; (4)-0.05 μA cm^{-2}

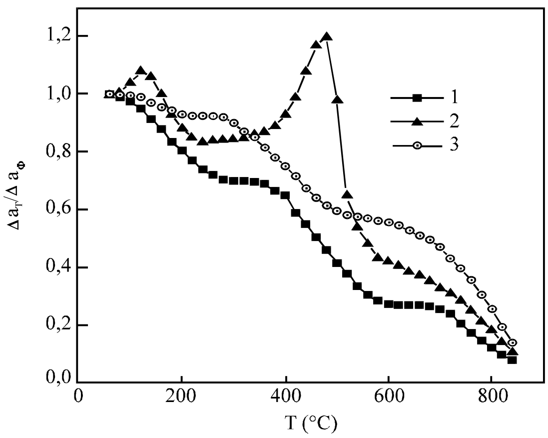

Fig. 2: Lattice Constant Recovery at Isochronal 15 min Annealing of Implanted Silicon. Δa_{Φ}-Change of Lattice Constant after Ion Implantation with Fluence Φ; Δa_T-Change of Lattice Constant after Ion Implantation and Annealing at Temperature T.-Si:P, ρ_0 = 0.5 Ω cm; (2)-Si:B, ρ_0 = 0.005 Ω cm; (3)-Si:B, ρ_0 = 0.005 Ω cm, Annealing with Electron Illumination

The stage at 700-900°C is characteristic for silicon implanted with B^+ ions only and may be explained by annealing of radiation defect complexes which include boron atoms.

In silicon heavily doped with boron the stages of "inverse" annealing at temperatures of 100-120 and 380-500°C are superimposed to the curves of the lattice constant recovery (Fig. 2, curve 2). However, for the same samples, the curves of isochronal annealing with electron illumination have not the "inverse" stages (curve 3).

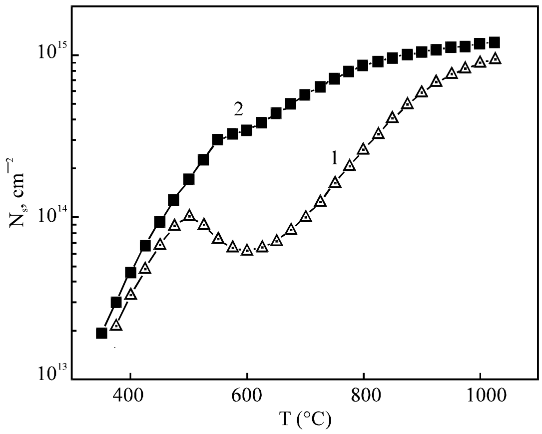

Fig. 3: Curves of Electrical Activation of Ion-implanted Boron in Silicon by Isochronal Annealing without (1) and with Electron Illumination (2)

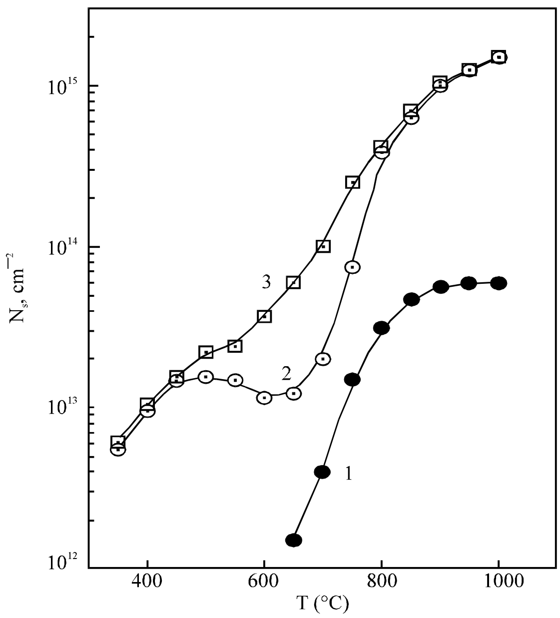

Fig. 4: Curves of Electrical Activation of Ion-implanted Phosphorus in Silicon by Isochronal Annealing: (1)-$\Phi_P = 6.3 \times 10^{13}$ cm^{-2}; (2)-$\Phi_P = 1.5 \times 10^{15}$ cm^{-2}, then Annealing and $\Phi_{Si} = 1 \times 10^{14}$ cm^{-2}; (3)-the same as (2) but Annealing with Electron Illumination

Figure 3 presents curves of electrical activation of implanted boron in silicon (the dependence of sheet concentration of the charge carriers N_s on the temperature of isochronal 15 min annealing) without (curve 1) and with (curve 2) simultaneous 10 keV electron irradiation with a current density of 5 μA cm^{-2}. The boron activation curve contains a stage of "reverse" annealing (curve 1).

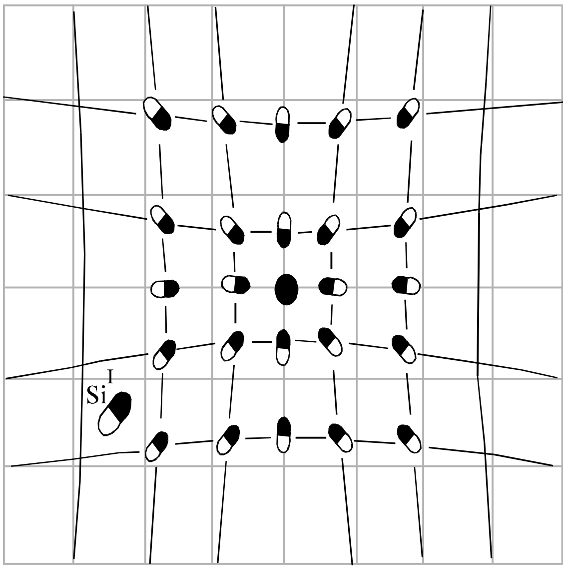

Fig. 5: Motion of Interstitial Si Atom under Elastic Deformation Field

In the case of boron activation during thermal treatment with simultaneous electron illumination only a bend is observed in the activation curve (curve 2).

The electrical activation of implanted phosphorus is shown in Fig. 4. The phosphorus activation curves do not contain stages of "reverse" annealing usually (curve 1). At the high P fluences ($>6\times10^{14}$ cm^{-2}) amorphization of silicon layer takes place and electrical activation of the impurity during the annealing occurs simultaneously with the recrystallization process. However, "reverse" annealing was present (curve 2) if the samples have been implanted with a high influence of phosphorus ions and then subsequently annealed to recrystallize amorphus layer and irradiated with Si^+ ions to generate the radiation defects. But the "reverse" stage is absent if the thermal treatment is carried out with simultaneous electron irradiation (curve3).

The greater increase of lattice constant resulting from implantation (Fig. 1) in heavily boron doped silicon as compared to n-type silicon crystals cannot be explained by the higher concentration of radiation defects. It has been ascertained in backscattering studies [10] that the presence of boron atoms does not influence the rate of introduction of stable defects in silicon crystals. The boron atoms participate probably in the formation of thermally stable complexes (stage at 700-900^{o}C) during annealing. We suggest that the additional increase of lattice constant in silicon heavily doped with boron may be connected with replacement of boron atoms from the nodes by self-interstitials generated during implantation. Boron atoms positioned at the nodes compress the lattice of silicon. The covalent radius of Si atom is 0.1175 nm, while for B-0.08 nm. The lattice constant is growing as the boron atoms are displaced from the nodes. The concentrations of replaced B atoms may be estimated from the differences in Δa and in the covalent radii of Si and B atoms. At the B^+ ion fluence of 2×10^{14} cm^{-2} the concentrations of displaced boron atoms from the nodes are estimated to be 8×10^{17}, 5.9×10^{18} and 2×10^{19} cm^{-3} at ion current densities of 0.5, 0.2 and 0.05 μA cm^{-2}, accordingly. The initial boron concentration in silicon samples was 4×10^{19} cm^{-2}. With decreasing of ion current density the quantity of boron displacements increases. This effect is joined with a level of ionization in implanted layer. It correlates with results on defects annealing (Fig. 2). The stages of "inverse" annealing are due to substitution of boron atoms in the lattice nodes by interstitial Si atoms. The temperatures of "inverse" annealing coincide with the annealing temperatures of interstitial complexes Si-P6 [11] and Si-B3 [12]. With increasing ionization level in the layer (electron illumination) the substitution process is suppressed (Fig. 2, curve 3).

Concerning activation process, it was shown using channeling method and electrical measurements [13] that the "reverse" stage in the activation curves is obliged to the boron displacement from the lattice nodes by interstitial Si atoms generated during the annealing of the interstitial complexes. At high concentrations of impurity and radiation defects, this process is seen in the curves of electrical activation of inserted phosphorus too. However, in the cases of boron and phosphorus the process of Watkins substitution is suppressed at high level of ionization in implanted layer. It follows from both X-ray diffraction and electrical investigations.

According to the ideas developed in work [14], the Watkins substitution is determined by the movement of interstitial Si atoms toward impurity atoms in the elastic strain field generated by these impurities due to misfit of the covalent radii of impurity and lattice atoms. 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 polarized 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 Si atom moves to a compression (dilatation) centre. This movement is schematically presented in Fig. 5. But what is the reason of the suppression of the substitution process when the level of ionization in the implanted layers is high? First, it must be considered from the point of view of charge states of interacting species. Boron and phosphorus impurities being located in the Si lattice nodes have opposite charge states. If the self-interstitials capture any type of nonequilibrium charge carriers (electrons or holes) it cannot suppress substitution process in the equal degree for both impurities (boron and phosphorus). The same results for

B and P atoms having the opposite charge states in the nodes, demonstrates that the reason of the substitution process suppression is not conditioned by charge states of the impurities and self-interstitials. We believe that at the high level of ionization, the nonequilibrium electrons and holes screen the electric dipoles in the deformed sphere with the result that the motion of Si atoms in the elastic strain field generated by the node-situated atom is suppressed.

CONCLUSION

The presented results of the X-ray diffraction and electrical investigations show that efficiency of displacement of boron atoms from the lattice nodes by self-interstitials depends upon a level of ionization in implanted silicon layers. The substitution process may be suppressed at condition that the effective ion current density must be more than 0.5 μA cm^{-2} during 100 keV B^+ scanning beam implantation. During annealing the process of boron substitution may be suppressed using low-energy electron irradiation with electron current density of 5 μA cm^{-2}.

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