

Secondary Defect Reduction by Multiple MeV Boron Ion Implantation

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Reduction of secondary defects by using a multiple ion implantation method has been investigated. 3 or 4-step multiple ion implantation and annealing cycles are applied to silicon substrates with and without pre-annealing. Secondary defect densities are reduced in both samples with and without pre-annealing. The secondary defect density in a 4-step multiple-implantation into a pre-annealed sample is reduced over one decade compared with a single-implanted sample without pre-annealing. No anomalous diffusion is observed in the multiple-implanted sample. The defect size is decreased in the pre-annealed sample. Reduction of secondary defects by using multiple-implantation method depends on the annealing process of the damaged layer.

1. Introduction

Recently, MeV ion implantation technology has been studied because of its useful properties. There are several proposals for device applications¹⁻³). In applying MeV ion implantation to device fabrication, secondary defects must be controlled. Some studies were reported concerning the characteristics of secondary defects⁴). Tamura et al. investigated the annealing behavior of MeV B, P, and As ion implanted Si⁵). Recently, the interest of MeV implantation technology is shifting to defect control. However, few works have been published about reduction of secondary defects: for example, implantation into FZ Si substrate⁶) or DZ formed substrate⁷), additional Si implantation⁸) or C implantation⁹), and subsequent 2-step annealing¹⁰).

In the present work, we report on the reduction of secondary defects by using a multiple boron ion implantation method with and without pre-annealing the substrate.

2. Experiments

p-type (100) Czochralski (CZ) silicon wafers with oxygen concentration of $1.6 \times 10^{18} \text{ cm}^{-3}$ were used in this investigation. Some wafers were pre-annealed before high energy boron ion implantation to reduce oxygen concentration in the boron implanted layer. Pre-annealing was performed by a 3-step furnace annealing, and its condition was 800°C, 2 h (N₂), 1100°C, 5 h (dry O₂), and 1000°C, 9 h (dry O₂). All samples were oxidized with a thickness of 50 nm before boron implantation. 3 or 4-step high energy multiple-implantation and annealing cycles were carried out to reduce secondary defects. Finally, all samples were implanted with a total dose of $2 \times 10^{14} \text{ cm}^{-2}$. In the case of 3-step multiple-implantation, the doses of first and second implantation were $7 \times 10^{13} \text{ cm}^{-2}$ and the dose of third implantation was $6 \times 10^{13} \text{ cm}^{-2}$ and the annealing time for each step was 40 min at 1050°C. On the other hand, in the 4-step multiple-implantation, the dose of each step was $5 \times 10^{13} \text{ cm}^{-2}$ and the annealing time for each step was 30 min at 1050°C. Boron ions were implanted with an energy of

1.5 MeV at room temperature. Finally, after boron implantation, all samples were furnace-annealed at 1050°C in N₂ ambient for a total annealing time of 2 h.

Secondary defects were observed by scanning electron microscopy (SEM) after employing Wright etching at room temperature, and also by cross-sectional and plan-view transmission electron microscopy (TEM)

The oxygen concentration of the substrate after pre-annealing was measured by secondary ion mass spectroscopy (SIMS). Furthermore the boron profile of the 3-step implantation and annealing cycles was measured.

3. Results and Discussion

3.1 Multiple boron implantation into high oxygen concentration substrates

Fig.1 shows the etch pit density as a function of the number of implantation steps. As the number of steps increases, the etch pit density decreases. As the number of implantation steps increases, the dosage of each step decreases. Therefore, the decrease of dosage in each implantation step is effective for reducing defect density.

Multiple ion implantation is very effective for the reduction of defect density.

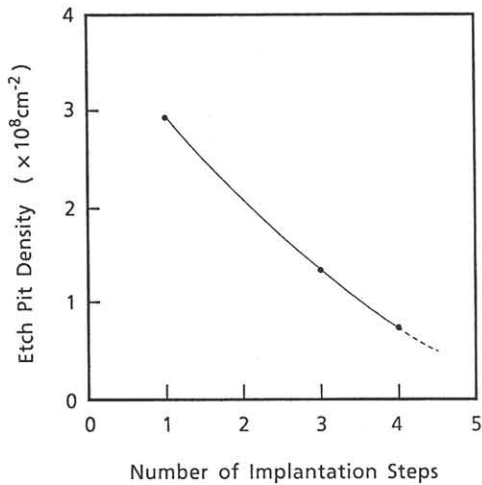


Fig.1 Dependence of etch pit density on number of implantation steps.

However, there are some possibilities that a change of boron profiles may occur during the implantation and annealing cycles. SIMS measurements were carried out. Fig. 2 shows the boron profiles measured for the 3-step multiple-implanted and single-implanted samples. Anomalous diffusion was not observed during the 3-step implantation and annealing cycles.

Typical examples of secondary defects observed in the multiple-implanted samples are shown in Fig. 3. Fig. 3 (a) and Fig. 3 (b) are TEM micrographs of 3-step multiple-implanted and single-implanted samples, respectively. Defects at a depth of about 2.5 μm from the surface are observed. From TEM micrographs, the defect density of multiple-implanted sample and single-implanted sample are $2.5 \times 10^7 \text{ cm}^{-2}$ and $1.3 \times 10^8 \text{ cm}^{-2}$, respectively. In the multiple-implanted sample, defect density is low. However, there are no advantages in the defect size of multiple-implanted samples in comparison with single-implanted ones.

Cross-sectional TEM micrographs of 3-step multiple- and single-implanted substrates are shown in Fig. 4 (a) and Fig. 4 (b), respectively.

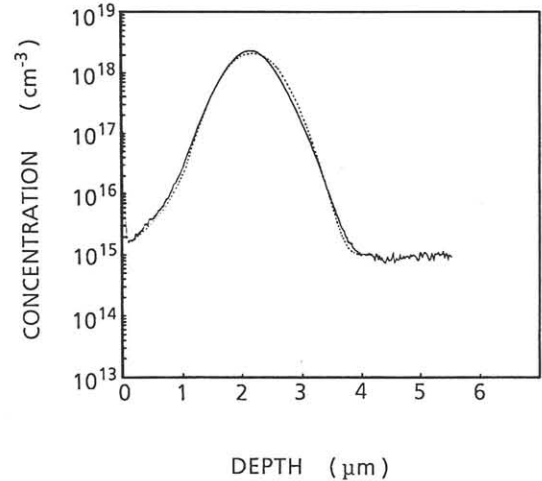


Fig.2 Depth profiles of boron implanted by 3-step multiple-implantation method (solid line) and single-implantation method (dotted line).

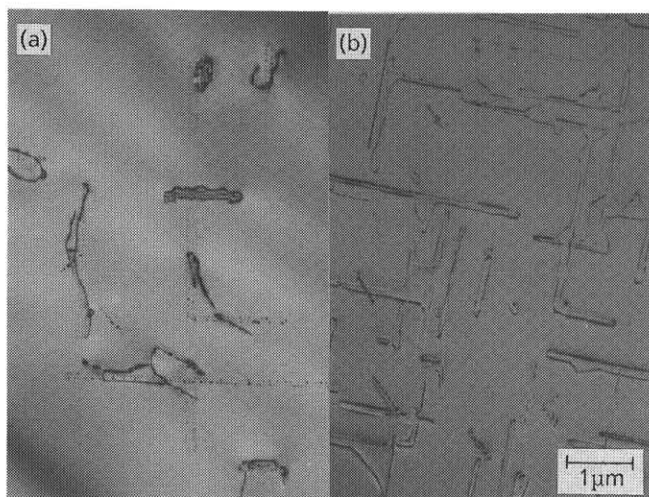


Fig.3 Plan-view TEM micrographs of secondary defects at a depth of 2.5 μm from the surface. (a) and (b) show samples with 3-step multiple-implantation and single-implantation, respectively.

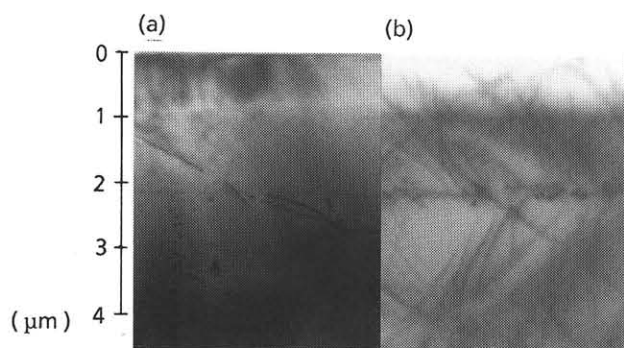


Fig.4 Cross-sectional TEM micrographs of a multiple-implanted sample (a) and a single-implanted sample (b).

The maximum density of secondary defects are located at a mean depth of 2.3 μm from the surface in both samples. Reduction of the defect density in the 3-step multiple-implanted substrate is confirmed also by observation in cross-sectional TEM micrographs. Secondary defects decreased more than 1/3 in the 3-step multiple-implanted substrate. However, the defect size is large in the 3-step multiple-implanted substrate compared with that in the single-implanted substrate. It is explained that implantation damage easily forms nuclei of secondary defects during the annealing process and recrystallization without secondary defect formation is difficult in the high oxygen concentration substrates. Therefore, perfect

recrystallization is not obtained in high oxygen concentration substrates even when implantation is carried out with lower dosages than $7 \times 10^{13} \text{ cm}^{-2}$ by using 3-step multiple-implantation. In the multiple-implantation method, some nuclei or secondary defects are formed during the first or second recovery process. Once nuclei or defects are formed during implantation into high oxygen concentration substrate, the secondary defects grow in the subsequent steps. Consequently, the reduction of defect size in the multiple-implanted sample may not occur. The multiple-implantation method is only effective for reduction of the defect density in high oxygen concentration substrate.

Therefore, it is necessary to suppress the growth of secondary defects during the annealing process.

3.2 Multiple boron implantation into pre-annealed substrates

The pre-annealing process is effective for the reduction of defect density and defect size⁷⁾. Hence, the pre-annealing process was used for suppressing the growth of secondary defects. The pre-annealing process was also employed to increase the effect of the multiple-implantation method. After pre-annealing, the oxygen concentration of the boron implanted layer lowers to $4 \times 10^{17} \text{ cm}^{-3}$ from $1.6 \times 10^{18} \text{ cm}^{-3}$ of the virgin silicon substrate. Plan-view TEM micrographs of defects in 4-step multiple- and single-implanted substrates with pre-annealing are shown in Fig. 5(a) and Fig. 5(b), respectively. The defect densities of the 4-step multiple- and single-implanted samples are $1.1 \times 10^7 \text{ cm}^{-2}$ and $3.4 \times 10^7 \text{ cm}^{-2}$, respectively. Finally, the defect density can be reduced over one decade by using a 4-step multiple-implantation into a low oxygen concentration substrate compared with a single-

implantation into a high oxygen concentration substrate as describe in section 3.1. In the 4-step multiple-implantation into low oxygen concentration substrates, shrinkage of defect size was observed. Mean size of the secondary defects is $0.39\ \mu\text{m}$ in the 4-step multiple-implanted substrate. However, the mean size of the secondary defects is $0.50\ \mu\text{m}$ in the single-implanted substrate, even using low oxygen concentration at the boron implanted layer.

Cross-sectional TEM measurements were carried out to observe the secondary defects in the vertical direction. Fig. 6 shows a cross-sectional TEM micrograph of secondary defects in 4-step multiple-implantation into pre-annealed substrate. Secondary defects are located at a mean depth of $2.5\ \mu\text{m}$. Size of secondary defects in the vertical direction are also reduced by using a low oxygen concentration substrate.

Reduction of the secondary defect density in the multiple-implantation method is also observed in pre-annealed substrates whose oxygen concentration is low enough. The out-diffusion of oxygen from the silicon substrate may be ignored during the multiple-implantation and annealing cycles.

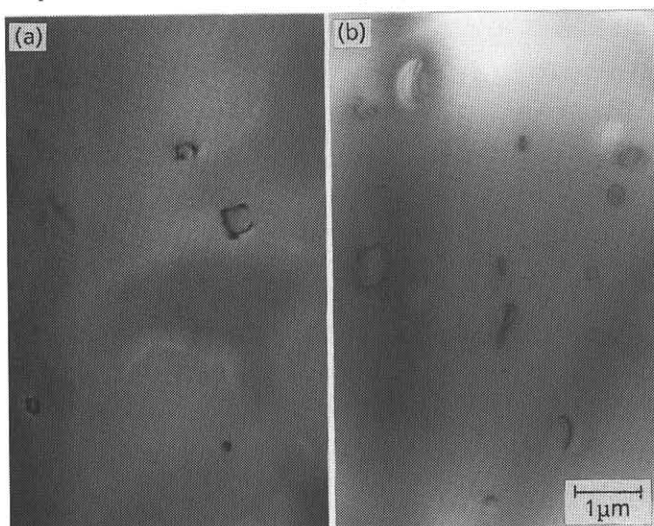


Fig.5 Plan-view TEM micrographs showing secondary defect. (a) and (b) are multiple- and single-implanted samples, respectively. Both samples are prepared by pre-annealing method to reduce oxygen concentration.

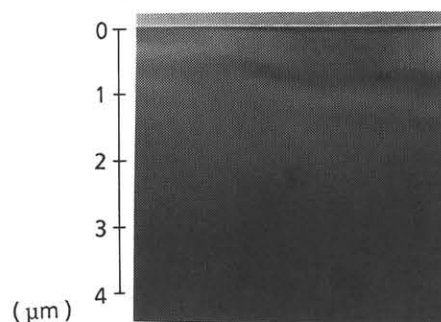


Fig.6 Cross-sectional TEM micrograph of 4-step multiple-implanted sample with pre-annealing

Therefore, secondary defects are reduced by the multiple-implantation effect. Reduction of defect density may not be caused by the reduction of the oxygen concentration during implantation and annealing cycles.

4. Conclusions

The multiple-implantation method is effective to reduce the secondary defect density and defect size. Defect density in the 4-step multiple-implantation into pre-annealed samples is reduced over one decade.

Acknowledgment

The authors gratefully thank Dr. T. Takemoto for his encouragement and support through this work. They also thank Prof. T. Ohzone for his useful discussion.

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