Anomalous Boron Depth Profile in Si Wafer with High Dose Ion Implantation

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A boron implanted Si wafer gets a lot of damage around a surface region under B^+ ion implantation. Amorphous / re-crystallized phase transformation takes place around the damaged region. Through this phenomenon, boron atoms segregate at the interface between a re-crystallized region and an amorphous region, which corresponds to the peak of B^+ by SIMS where the maximum peak of vacancies exists.

1. Introduction

A round-robin study was organized among Japanese SIMS users to evaluate the reproducibility of depth profiles and the linearity of the ion intensity using boron implanted silicon wafers with a variety of ion doses. In the round-robin study, quantitative analysis with RSD of 11% could be performed in the dose range from $3x10^{14}$ to $3x10^{16}$ ions / cm^2 [1]. And for higher doses, ($3x10^{16}$ - $1x10^{17}$), deviations of RSFs (Relative Sensitivity Factors) have been reported to result in a dip in the boron depth profile, dose dependence of Rp and variation of matrix ion intensity due to the boron binding state (e.g. clustering).
In these tests, there are two following anomalous phenomena in higher dose implanted materials ($3x10^{16}$ - $1x10^{17}$ ions/cm^2).

(1)There is a sharp bend where the maximum peak of vacancies exists (Dp) (Fig. 1).
(2)The emission of cluster ions drastically increases.

In this paper, we discussed about the point (1), an anomalous phenomenon, that a sharp bend appeared with the implanted dose range of $1x10^{17}$ ions/cm^2. Mizushima *et. al.* have reported that boron cluster, B_{12} would exist in boron implanted Si wafers with higher doses ($1x10^{17}$) [2,3]. Tomita *et. al.* also reported that secondary cluster ion emission probability changes due to formation of boron clusters in the sample [4]. We report the correlation between the crystal structure changes of implanted Si and an appearance of a sharp bend in the depth profile.

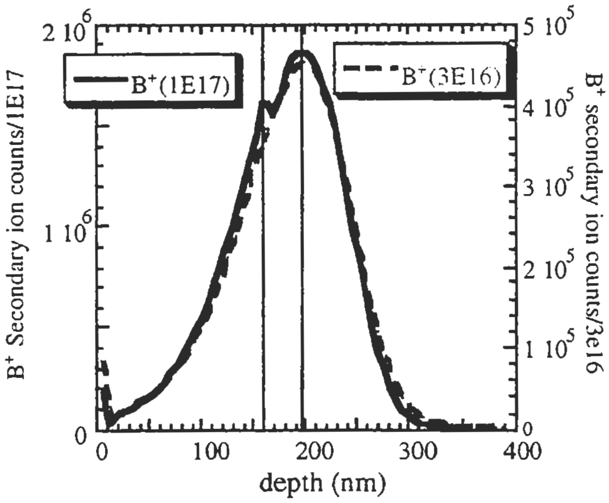

Fig. 1 Boron depth profiles as-implanted Si wafers with doses of $3x10^{16}$ and $1x10^{17}$ ions/cm^2.

2. Experimental

Four specimens were prepared to implant 50 keV $^{11}B^+$ into Si wafers with doses of $1x10^{15}$, $1x10^{16}$, $3x10^{16}$ and $1x10^{17}$ ions/cm^2 using AMT PI-9500(xR) ion implanter (Applied Materials Corp.) at room temperature. This apparatus controlled the temperature of the sample using water cooling. SIMS measurements were performed with CAMECA ims-4F to get boron depth profiles. And cross sectional transmission electron microscopy (XTEM) and ion channeling measurements taken by RBS (Rutherford Backscattering Spectroscopy) was applied for evaluation the crystallinity of the damage region of the samples by ion implantation. X-ray reflectivity measurements were done to evaluate the density of the upper-most surface of the samples.

3. Results

3.1 SIMS measurements

Fig. 1 shows the anomalous sharp bend in the boron depth profile with dose of $1\mathrm{x}10^{17}$ ions / cm^2 which is compared with that with $3\mathrm{x}10^{16}$. From the other SIMS measurements which could monitor oxygen with negative secondary ion detection using Cs$^+$ ion beam, it was found that no oxygen atoms piled up at the depth position which the sharp bend appeared. And we also monitored the work function changes by means of investigating the secondary ion energy distribution of boron. If boron clusters were produced and then changed the chemical state of silicon, secondary ion energy distribution would be shifted to reflect the work function change. Fig. 2 shows the energy distributions of boron secondary ions at various depth positions. Each depth position is described in the upper small figure in Fig. 3. No shifts in the energy distributions can be monitored.

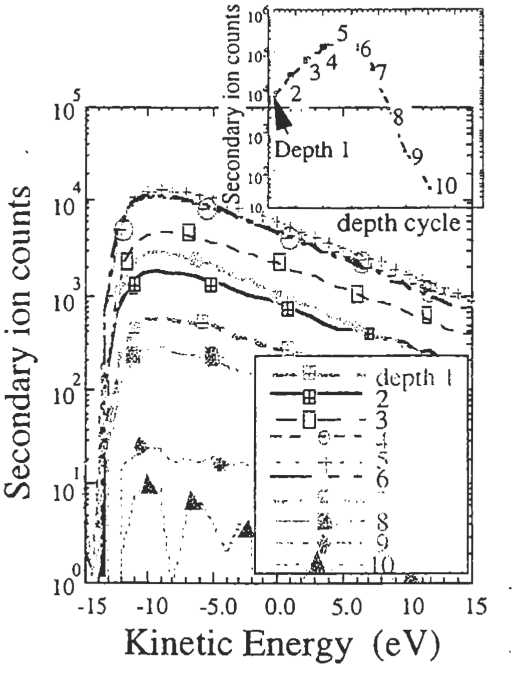

Fig. 2 Energy distributions of boron secondary ions at various depth positions

3.2 Ion channeling measurements

Fig. 3 shows the ion channeling spectra of boron implanted silicon wafers with various doses by using 2.0 MeV $^4He^{2+}$. Below dose range of $3\mathrm{x}10^{15}$ ions / cm^2, silicon wafers keep such a good crystallinity as a not-implanted wafer. On the other hand, over the dose range of $1\mathrm{x}10^{16}$ ions / cm^2, implantation induced defects appear around the Dp region. Furthermore, over the dose range of $3\mathrm{x}10^{16}$ ions / cm^2, a lot of defects are introduced into the Rp region.

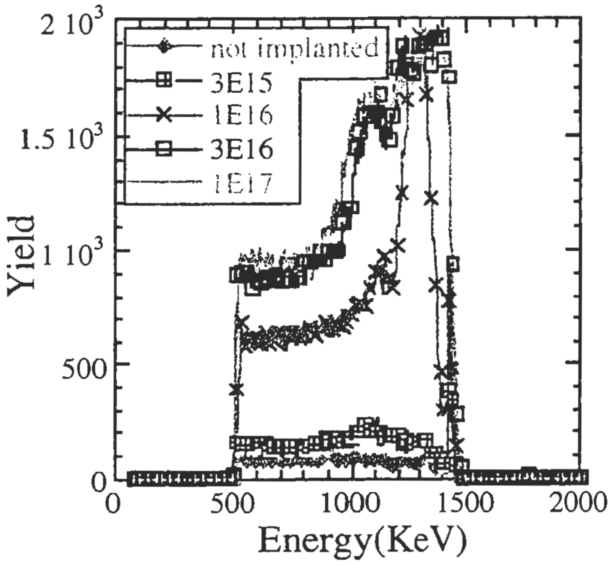

Fig. 3 Ion channeling spectra of boron implanted silicon wafers with various doses.

3.3 XTEM observations

Fig. 4 shows XTEM bright field image of the sample with the dose of $1\mathrm{x}10^{16}$ ions / cm^2 which has the damage region observed with the ion channeling measurements. In this photo also shown are boron and vacancy distributions obtained by TRIM-98 monte-carlo simulation.

Fig. 4 XTEM bright field image of boron ion implanted silicon wafer with dose of $1\mathrm{x}10^{16}$ ions / cm^2.

The picture presents the upper-most crystal layer / amorphous layer which contains Si(001) microcrystals / single crystalline silicon layer with a lot of dislocations / Si substrate. The amorphous layer is regarded as the damage region, *i.e. Dp,* which has the excess damage over the damage threshold for transformation of the crystalline silicon to the amorphous layer.

Fig. 5 shows XTEM image of the sample with dose of 1×10^{17} ions / cm^2. The picture presents the upper-most amorphous layer / the re-crystallized layer with a lot of dislocations / the amorphous layer which corresponds to Dp and Rp regions. We also observed the XTEM image of the sample with dose of 3×10^{16} ions / cm^2. This shows the amorphous layer covered the entire damage region which was between the top surface and the Rp. It indicated the amorphous layer was changed into the re-crystallized layer under the high dose of ion implantation, *i.e. hot implantation* . The re-crystallized layer would not be highly oriented to Si(001), which is expected from the ion channeling results.

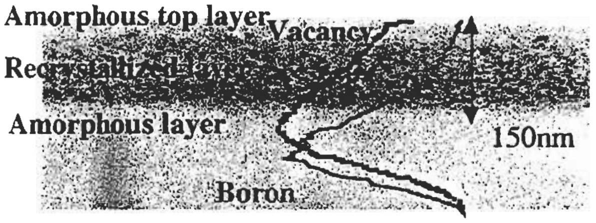

Fig. 5 XTEM bright field image of boron ion implanted silicon wafer with dose of 1×10^{17} ions / cm^2.

4. Discussion

From SIMS measurements, no matrix effects, which resulted from the existence of oxygen and/or the change of the chemical states of silicon crystals, appear in these systems. Therefore, the sharp bend is found to be due to segregation of boron. Ion channeling measurements and XTEM observations show that the crystal structure around damage regions drastically change, depending on the amounts of boron implanting doses.

From all the results, we assumed two diffrent reasons why the sharp bend appears in the boron depth profile.

(1) The amorphous layer would have a smaller density than that of the crystalline silicon.

And then the amorphous layer was changed transiently into recrystallized layer with higher doses. It is because that the stopping power of boron ions into silicon substrate would drastically change and finally the sharp bend would appear.

(2) During ion implantation, an amorphous / re-crystallized phase transformation would drastically take place. This reaction would accompany the boron segregation. Since no more than 5 atomic % of boron cannot be solved in the single crystalline silicon, boron segregates at the interface between the amorphous layer and the re-crystallized layer. The driving force of the segregation is the amorphous / re-crystallized phase transformation.

In order to make the formation mechanism of the sharp bend clear, X-ray reflectivity measurements are performed to decide the density of the surface layer. As the results, any density changes which would affect the boron stopping power to silicon substrate cannot be observed at all.

Therefore, we conclude that the formation mechanism of the sharp bend is due to the boron segregation accompanyed by the amorphous / re-crystallized phase transformation.

5. Conclusion

The formation mechanism of the anomalous sharp bend in the boron depth profiles has been studied. It is only observed the sample in which boron is implanted with dose of 1×10^{17} ions / cm^2. The crystal structure around damage regions drastically change for high dose boron imlanted samples, depending on boron implantation doses.

We conclude that the sharp bend is due to the boron segregation accompanyed by the amorphous / re-crystallized phase transformation based on SIMS, RBS, XTEM and X-ray reflectivity measurements.

We, however, have not discussed how this phenomena affect the deterioration against the boron quantification yet. Furthemore, we must precisely investigate the sputtering rate change, the change of secondary ion emission probability involving the cluster ion emission through the amorphous / re-crystallized layer system.

These analytical difficulties also apply in the evaluation of the very shallow ion-implanted sample, which contains no more than 5% boron and a lot of defects, by SIMS measurements even though an ultra-low energy ion beam is used.

6. References

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