Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 101-104 **A-7-2**

Annealing of Defects by High Energy Ion Implantation

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Annealing of defects caused by high energy ion implantation was investigated mainly by photoluminescence (PL) spectroscopy. The 15 minute isochronal annealing behaviors of defects were divided into three temperature ranges, between 450 - 1200°C. Defects in low dose sample could be annealed out by high temperature annealing. Remaining defects in higher dose samples could be reduced to some extent in two step annealing. Dopant profiles have also been studied by SIMS. An anomalous oxygen layer was found at Rp, where dislocation loops were located.

1. Introduction

High energy ion implantation has a lot of advantages, achieved through forming a high concentration layer a few microns deep from a silicon surface. By this technology, it is possible to make devices with new structures, such as retrograde wells and buried grids/planes. However, heavy lattice damage is created by high energy ions. Some studies[1-3] have been reported about a distribution of dopants and defect annealing. Most of them have come to the conclusion that it is not easy to recover complete crystal perfection of silicon damaged by ion implantation. It is necessary to study annealing behavior of defects in detail, to appropriately utilize this technology for devices which are sensitive to residual defects.

2. Experimental and discussions

P-type (100) silicon wafers were implanted with 0.8 or 1.5 MeV phosphorus ions. Its dose was 10^{12}-10^{15} cm^{-2}. Annealing was carried out at 400 - 1200°C for 15 - 60 minutes in a nitrogen ambient. Defects were detected by photoluminescence (PL) spectroscopy, and observed by cross section transmission electron microscope (XTEM).

The PL technique is quite sensitive to point defects or its clusters, and also to low density defects. By this PL technique, defect behaviors in 15 minute isochronal annealing could be classified into three temperature ranges. Figure 1 shows three typical PL spectra for each range. In a low temperature range (below 550°C), point defect clusters, such as I1 (1.018eV: five

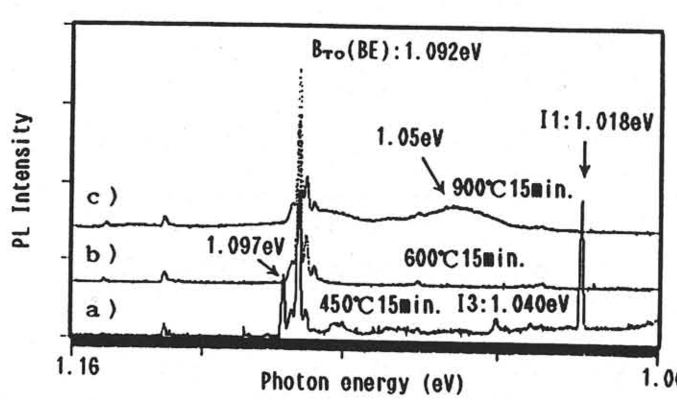

Fig.1 Photoluminescence spectra of 1.5MeV 1×10^{15} cm^{-2} phosphorus implanted silicon after 15 minute isochronal annealing at various temperature: a) 450°C, b) 600°C, c) 900°C

vacancies), I3 (1.039eV: multivacancies)[4] and others (1.097eV etc.), whose assignments are not known yet, were detected (Fig.1 a). In a mid-temperature range (600°C - 700°C), PL spectra did not exhibit any significant defects and indicated apparently complete annealing of point defects clusters (Fig.1 b). PL lines in fig.1 b are due to implanted phosphorus, boron in the raw p-type wafer in addition to other lines which were also observed in a raw wafer heat treated simultaneously with the implanted wafers. In a high temperature range (above 800°C), new forms of defects were observed at 1.05, 1.08 and 1.14eV(Fig.1 c).

These PL lines, observed in the high temperature range, have neither been reported nor assigned yet. Their peak positions were shifted, according to ion implantation and following annealing conditions. The 1.08eV peak shifts, which reflect implantation conditions, are shown in Fig.2. In Fig.2, the vertical axis is the peak position of each sample, represented by individual marks and the horizontal axis is an annealing temperature. Peaks marked by open symbols were shifted linearly toward higher energy, when annealing temperature was above 1000°C. Peak positions of 1.5MeV and 0.8MeV ion implanted samples were the same, but that of 150keV ion implanted sample was 3-5meV lower. However, peak positions of 1.5MeV 1×10^{15} cm^{-2} (closed circle) had a maximum at 1000°C annealing. This was characteristic of high energy and high dose ion implantation. Shifts by the 1.14eV peak were very similar to that for 1.08eV peak, but not that for the 1.05eV peak, as shown in Fig.3. Peak positions of 1.05eV peak shifted almost the same, having a minimum at 1100°C in all samples but the low energy (150keV) implanted one, in which there were a little shifts toward lower energy above 1000°C. These peak shifts suggest that two kinds of defects were dominant in high temperature annealing.

In low dose sample (2×10^{12}cm^{-2} at

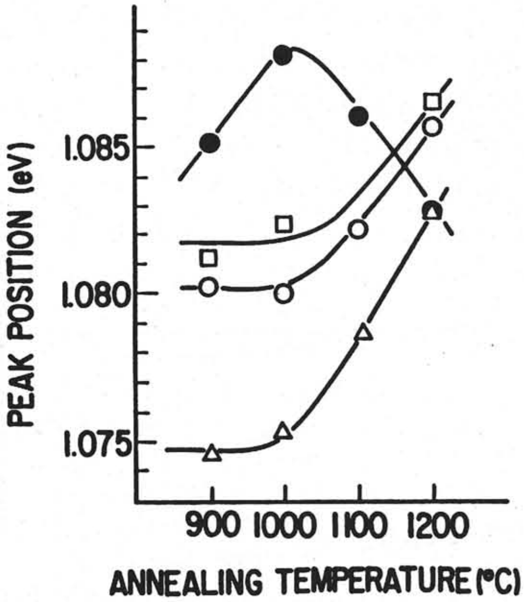

Fig.2 Shifts in the 1.08eV peak position, according to implantation and annealing conditions.

△ 150keV 6×10^{13}cm^{-2}
○ 0.8MeV 6×10^{13}cm^{-2}
□ 1.5MeV 6×10^{13}cm^{-2}
● 1.5MeV 1×10^{15}cm^{-2}

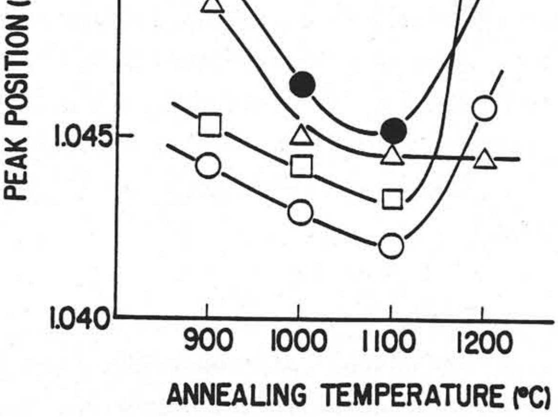

Fig.3 Shifts in the 1.05eV peak position, according to implantation and annealing conditions.

1.5MeV), almost none of these peaks were observed in a high temperature range in spite of its high energy implantation. The PL spectra of silicon implanted at 1.5MeV with different dose after 1200°C annealing, are shown in Fig.4. Peaks at 1.05eV, 1.08eV and 1.14eV of a low dose ($2x10^{12}cm^{-2}$) sample could be completely annealed out, though these peaks of high dose samples became more marked.

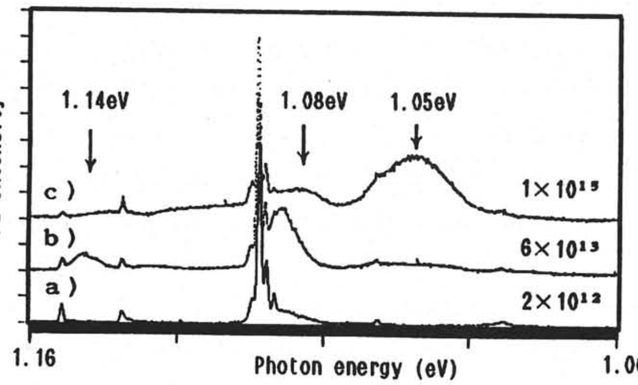

Fig.4 Photoluminescence spectra of silicon annealed at 1200°C for 15 minutes. Phosphorus doses implanted at 1.5MeV are as follows;

a) $2x10^{12}cm^{-2}$, b) $6x10^{13}cm^{-2}$, c) $1x10^{15}cm^{-2}$

Defects growth or shrinkage, during the VLSI processes, are very important. As indicated in Fig.1, making use of a mid-temperature as the pre-annealing, better results would be expected for developing a defect-free process by a two step annealing. Experiments on two step annealings were made, in which the second step condition was fixed to 1000°C for 60 minutes and the pre-annealing conditions were changed. Figure 5 shows the PL spectra of 1.5MeV $6x10^{13}cm^{-2}$ phosphorus implanted silicon with and without pre-annealing at 450°C or 600°C. These PL spectra shows the pre-annealing effect at the different temperature. Unexpectedly, the pre-annealing at a mid-temperature did not decrease the defects caused after the second 1000°C annealing. However the pre-annealing at a low tempera-

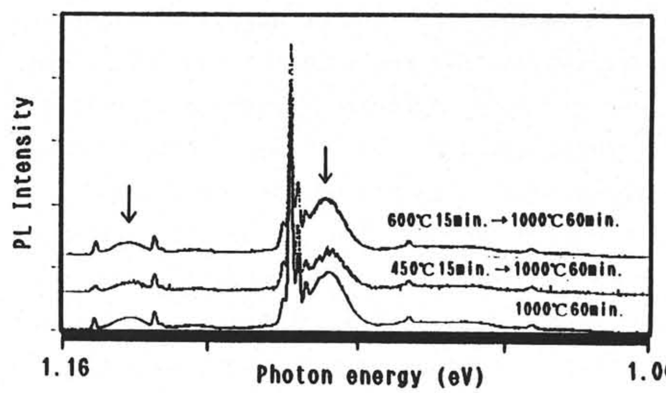

Fig.5 Photoluminescence spectra of 1.5MeV $6x10^{13}cm^{-2}$ phosphorus implanted silicon after two step annealing.

ture decreased them to 3/4 of those without pre-annealing. In some cases the pre-annealing decreased them to almost half. Annealing at a mid-temperature must leave damages which are not observed by PL, because of their non-radiative characteristics. Those non-radiative residual damage became observable by PL as a result of second high temperature annealing.

The distribution of implanted dopants is another item of interest in the high energy ion implantation technique, which would be an important element for device designs. Phosphorus and oxygen profiles were measured by SIMS and are shown in Fig.6. Since the dopant profile calculations are often tried using Person IV function[5], the authors have also made an attempt to express

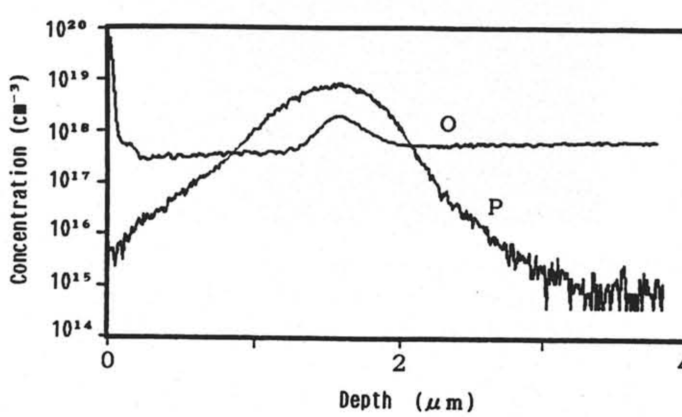

Fig.6 SIMS spectrum of 1.5MeV $1x10^{15}cm^{-2}$ phosphorus implanted silicon and annealed at 1000°C for 15 minutes.

the dopant profiles of high energy ion implantation. For as implanted samples, there was a good agreement between calculation results and SIMS profiles, if appropriate parameters were picked for calculation. If annealing has been done, a redistribution of dopants make profiles broader and discrepancy between calculated and actual profiles becomes significantly bigger. In the case of 1200°C annealing for 15 minutes, the surface concentration increased very much. It was impossible to express the dopant profiles by Pearson IV function. One interesting feature found was an anomalous oxygen layer at the Rp (projected range) in samples where dislocation loops were observed at Rp by cross section transmission electron microscopy (XTEM). Figure 7 shows an XTEM photograph of 1000°C 15 minute annealed silicon, implanted at 1.5MeV with its dose $1X10^{15}cm^{-2}$. This was found, at this moment, only in a sample in which dislocations were observed at Rp. This anomalous layer may be oxygen gettered at dislocation loops. Because of their fixed location, there are possibilities to utilize them for gettering.

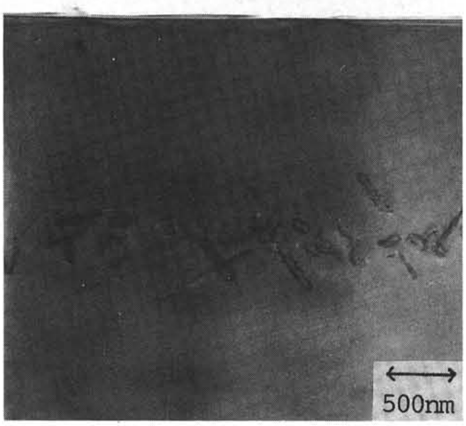

Fig.7 XTEM photograph of 1.5MeV $1x10^{15}cm^{-2}$ phosphorus implanted silicon and annealed at 1000°C for 15 minutes.

3. Summary

Annealing behaviors for defects, induced by high energy phosphorus ion implantation, were divided into three temperature ranges; low temperature, below 550°C for point defects cluster formation, and mid-temperature, at 600 - 700°C, for apparent annealing out point defects and high temperature above 800°C for creating defects in high dose samples.

By PL analysis there is a critical dose between $2x10^{12}$ and $6x10^{13}cm^{-2}$ for annealing out defects by high temperature annealing. Defects in a low dose sample could be annealed out. However, in higher dose, three PL peaks were observed in the high temperature range.

The behavior of these peaks was related to ion implantation conditions. From this behavior, it was concluded that there were two kinds of defects.

Two step annealing definitely indicates a reduction in defects by low temperature pre-annealing process. Although pre-annealing effects were fairly limited, this will be a good starting point to develop sophisticated processes for defect-free annealing.

The new layer, with a high oxygen concentration, was found at Rp, where dislocation loops were located.

This detailed study on defect annealing will contribute to establishing a high energy ion implantation technology, by which devices with new structures can be developed.

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