Mechanism of Intrinsic Gettering of Iron in Silicon

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We present a new experimental approach to using intrinsic gettering to remove Fe impurities. After isochronal and isothermal annealing followed by quenching, we measured the change in the Fe concentration, [Fe-B] + [Fe_i], near surface using DLTS. An ideal temperature and minimum annealing time exist for removing the Fe contamination by intrinsic gettering. The temperature is lower than the solid solubility temperature, that is, Fe is supersaturated. The degree of the supersaturation is one order of magnitude. The time is ten times longer than that required for Fe to diffuse to the defect region.

1. Introduction
It is well known that Fe impurities are the principal device performance degrading contaminants in VLSI fabrication\(^\text{(1)}\). These impurities are difficult to remove with intrinsic gettering (IG)\(^\text{(2)}\). IG technology is used in VLSI fabrication. But the mechanism of IG has not been clarified. We think that a thorough examination of the gettering temperature and time is important. We annealed samples both isochronally and isothermally followed by quenching, then measured the change in the Fe concentration, [Fe-B] + [Fe_i]\(^\text{(3,4)}\), near surface using DLTS. We discussed the IG mechanism and propose an optimized annealing treatment to remove the Fe impurities.

2. Experiments
The sample wafers were Czochralski (CZ) and float zone (FZ) grown, (100), p-type, boron-doped, and 10 ohm-cm. Some sample wafers were annealed in a three-step procedure to form both a denuded zone (DZ) and an oxygen precipitated region. All wafers were contaminated with a NH\(_4\)OH-H\(_2\)O\(_2\)-H\(_2\)O mixture containing 100 ppb Fe. The surface concentration of Fe was determined by atomic absorption spectrophotometry with the HF vapor phase decomposition around 3.2 x 10\(^{13}\) cm\(^{-2}\). The wafers were cut in 25 by 15 mm and were annealed at 1150°C for 30 min to promote Fe diffusion. We measured the Fe concentration near surface using DLTS.

3. Results and Discussion
The crystal-defect depth profile of the wafers annealed for IG were observed beveling the wafer at 5°44’ and then Secco etching, for 2 min. The DZ width in the CZ wafers was about 20 um invariant of annealing time for IG. The defect density in a wafer with long-time IG was about ten times that of a wafer with IG. Figure 1 shows the Fe concentration difference in Fe concentration between quenching and slow cooling.

![Fig. 1 Difference in Fe concentration between quenching and slow cooling.](image-url)
of each sample, comparing those with no IG, with IG, and with long-time IG after annealing at 1150°C for 30 min in nitrogen (N₂), followed by quenching in boiling water or slow cooling in air. When quenched, the Fe concentration is almost the same for samples at 5.0 to 4.0 x 10^14 cm⁻³. However, for slow cooling, the concentration of the IG wafer is 1/3 and of the long-time IG wafer 1/4 of that of a wafer with no IG. This result suggests that gettering removes impurities during cooling from 1150°C to room temperature.

We examined the temperature region in which gettering occurs. We annealed samples at 1150°C for 30 min followed by quenching, then at 850 or 900°C, for 20 s followed by a second quenching. Figure 2 shows the results.

![Fig. 2](image)

**Fig. 2** Dependence of Fe concentration on annealing temperature.

At 850°C, the Fe concentration in the samples with IG reduces to 1/3 of that in the sample with no IG and to 1/5 with long-time IG. At 900°C, the Fe concentration in the samples with IG reduces to 1/2 of that in the sample with no IG and to 1/3 with long-time IG. This reduction is due to gettering. The dominant effect is caused by oxygen precipitates, less significant is the homogeneous precipitation of Fe into a FeSi₂ phase at 850 and 900°C(5).

In addition, we annealed some samples at 1150°C for 30 min followed by isothermal annealing at a temperature between 800 and 900°C and then quenching. Figure 3 shows the result of annealing at 900°C. The figure also shows a result from an FZ wafer. After annealing for 20 s, the Fe concentration in the FZ wafer and the wafer with no IG are about 3 x 10^14 cm⁻³, the same as a quenched wafer annealed at 1150°C. In contrast, the Fe concentration in a wafer with IG reduced to 1/2 and in the long-time IG-process wafer, to 1/3. The gettering takes less time as the density of oxygen precipitates increases. After annealing for 30 s, the Fe concentration in the wafers with IG and long-time IG-process wafer reduces to 1/6 of that for a sample quenched from 1150°C. Gettering stops after 30 s when the Fe concentration in the demounded zone reduces to the solid solubility limit, at 900°C, of 4 x 10^13 cm⁻³ (6). The diffusion time of Fe at 900°C over 20 μm of D₂ width is 2.6 s, about 1/10 of 30 s. Thus, this suggests that the removal of the Fe contamination by gettering requires a time for diffusing and reacting with the oxygen.

![Fig. 3](image)

**Fig. 3** Dependence of Fe concentration on annealing time at 900°C.
precipitates in the defect region. We believe that Fe precipitates into FeSi2 in both an FZ wafer and a wafer with no IG. The Fe concentration decreases in these wafers somewhere between 30 and 600s. In addition, the Fe concentration in an FZ wafer and a wafer with no IG will reach a limit of 4 x 10^{13} cm^{-3} after more than 600s of annealing. This is the solid solubility limit at 900°C.

By using Secco etching for 2 min, we observed the precipitation of FeSi2 on all wafers annealed for 10 min at 900°C. Surface precipitates caused by Fe contamination were observed as shallow pits on an FZ wafer and the wafer with no IG but no precipitates could be observed on the wafer with IG or long-time IG. Figure 4 shows photographs of an FZ wafer and the wafer with long-time IG.

4. Conclusion

There is an ideal temperature and minimum annealing time for the removal of Fe contamination by gettering. The temperature is one order of magnitude lower than the solid solubility temperature and the time is about ten times longer than that required for Fe to diffuse to the defect region. For example, for Fe concentration at 3 x 10^{14} cm^{-3}, the ideal temperature is 900°C and the time is about 30s. It is possible to further improve the efficiency of contamination removal by controlling the wafer cooling rate.

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References