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Intrinsic Gettering of Iron Impurities in Silicon Wafers

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We present a new experimental approach to using intrinsic gettering to remove Fe impurities. We annealed samples, followed by quenching, and measured the Fe concentration near the surface using deep-level transient spectroscopy. The supersaturation of Fe impurities is necessary for the intrinsic gettering of Fe. However, for a higher supersaturation, Fe impurities precipitate faster than gettering. The optimum degree of supersaturation is one order of magnitude. Gettering is limited by the reaction of Fe with the oxygen precipitates in the defect region, rather than by Fe diffusion to the defect region.

KEYWORDS: silicon wafer, intrinsic gettering, iron, oxygen precipitate, deep-level transient spectroscopy, solid solubility, diffusion

§1. Introduction

As devices become smaller, it is increasingly important to reduce the heavy-metal impurities in the active regions to prevent fluctuations in device characteristics.¹⁾ Fe impurities are known to be the principal contaminant that degrades device performance. These impurities are hard to remove with intrinsic gettering (IG)*, and the exact mechanism of IG has not been clarified. Miyazaki *et al.* reported that gettering efficiency for Fe is improved by heat treatments, ending with low-temperature annealing at 650°C.²⁾ They evaluated the gettering efficiency by the MOS C-t method. Weber and Gilles³⁾ and Gilles *et al.*⁴⁾ proposed the model of intrinsic gettering as follows. During a high-temperature annealing in which contamination by heavy-metal impurities occurs, these impurities are distributed uniformly in the defect region and the denuded zone and no gettering occurs. Upon lowering the temperature, the impurities become supersaturated and they precipitate very rapidly in the defect region but not in the denuded zone. The resulting concentration gradient is the driving force for diffusion into the defect region, which is the actual gettering step. They derived this intrinsic gettering model from an analysis of the precipitation behavior of Fe between 200°C and 300°C using electron spin resonance. They did not measure the Fe concentration in the denuded zone and calculated the gettering time as that required for Fe to diffuse to the defect region. We believe that a thorough examination of the gettering temperature and time are important to study the gettering mechanism, so we directly and quantitatively evaluated the gettering process of Fe by measuring the Fe concentration in a denuded zone after isothermal annealing at several temperatures followed by quenching using deep-level transient spectroscopy (DLTS).⁵⁾

§2. Experiments

Silicon wafers were Czochralski-grown, (100), boron-

doped, and 10 ohm-cm. Some wafers were annealed in a three-step gettering process (high, low, and high temperature) to form a denuded zone and an oxygen-precipitated region.⁶⁾ High temperature is 1100°C and low temperature is 650°C. We also prepared long-term gettered wafers by lengthening the low-temperature annealing time. All wafers were contaminated by immersing in a $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ mixture containing Fe. The surface concentration of Fe was determined by atomic absorption spectrophotometry with the HF vapor-phase decomposition⁷⁾ around $3.2 \times 10^{13} \text{ cm}^{-2}$. Sample wafers were cut into 25 by 15 mm pieces and annealed at 1150°C for 30 min to provide Fe indiffusion. We then annealed the samples at 800–900°C and for 20–600 s in N_2 followed by quenching in boiling water. For DLTS measurements, an Al Schottky contact was evaporated at the surface of the samples. Ga was rubbed on the back surface to produce an ohmic contact. We measured the change in the Fe concentration, $[\text{Fe-B}] + [\text{Fe}_i]$,⁸⁻¹⁰⁾ near the surface using DLTS. The reverse bias is 5 V and injection pulse width, 1 ms. The rate-window is set to 1000 s^{-1} . We observed crystal defects at the surface by Secco etching¹¹⁾ for 2 min. The crystal-defect depth profiles of the wafers annealed for the three-step gettering process were also observed by beveling the wafer at $5^\circ 44'$ and then Secco etching for 2 min.

§3. Results and Discussion

Figure 1 shows the typical DLTS spectrum after about 24 h storage at room temperature for a sample diffused with Fe. The dominant feature in the DLTS spectrum was, in all cases, the Fe-B pair state. We calculated the Fe concentration as the Fe-B pair concentration plus the interstitial iron (Fe_i) concentration.⁸⁻¹⁰⁾

Figure 2 shows the Fe concentration in nongettered, gettered (IG), and long-term gettered samples after annealing at 1150°C for 30 min in N_2 , followed by quenching in boiling water or slow cooling in air. For quenching, the Fe concentration is almost the same as samples at 3.0 to $4.0 \times 10^{14} \text{ cm}^{-3}$. However, for slow cooling, the Fe concentration in the gettered wafer is 1/3 and, for the long-term gettered wafer, 1/4 that of the nongettered wafer. This suggests that gettering occurs during cooling

*T. Abe and T. Ito: Extended Abstracts of the 36th Spring Meeting of the Japan Society of Applied Physics and Related Societies, Chiba, March, 1989, 1a-M-2.

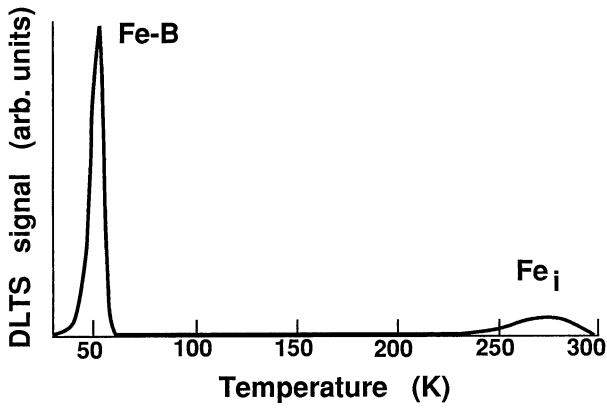


Fig. 1. Typical DLTS spectrum after about 24 h storage at room temperature for a sample diffused with iron.

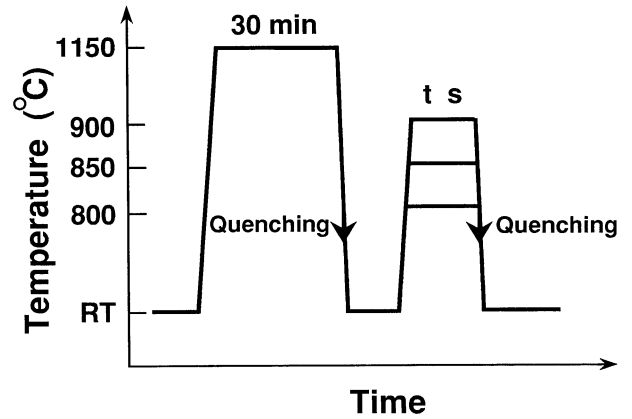


Fig. 3. Annealing sequence.

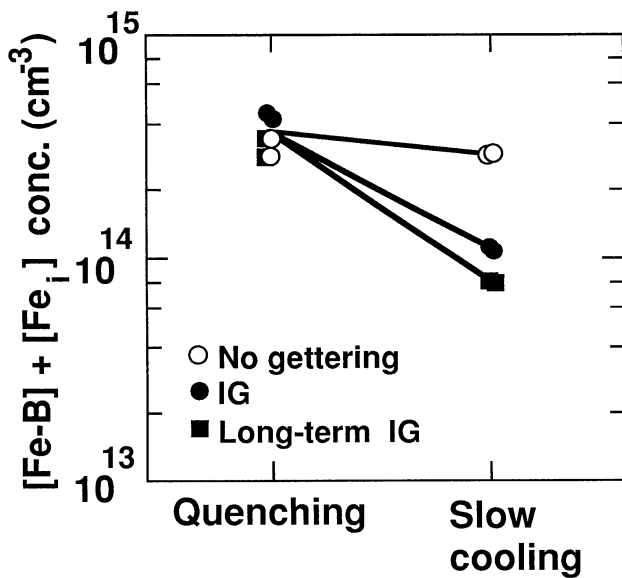


Fig. 2. Difference in Fe concentration between quenching and slow cooling.

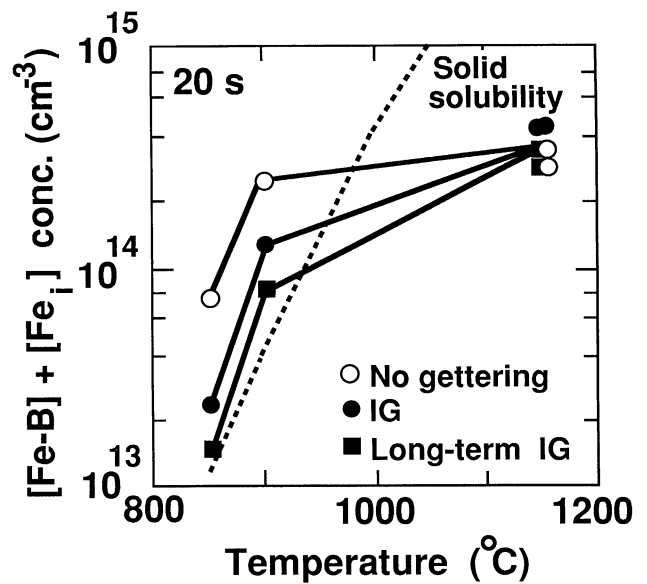


Fig. 4. Dependence of Fe concentration on temperature in annealing for 20 s.

from 1150°C to room temperature. The denuded zone is about 20 μm , irrespective of annealing time for the three-step gettering process. The defect density in a gettered wafer is about $5.0 \times 10^5 \text{ cm}^{-2}$ and, for a long-term gettered wafer, $5.0 \times 10^6 \text{ cm}^{-2}$.

We studied the temperature region in which gettering occurs and the gettering process. Figure 3 shows the annealing sequence. We annealed samples at 1150°C for 30 min in N_2 followed by quenching, then isothermally annealed them at 800, 850, or 900°C, followed by quenching. Figure 4 shows the dependence of the Fe concentration on temperature in annealing for 20 s. At 850°C, the Fe concentration in the gettered wafer drops to 1/3 and, for the long-term gettered wafer, to 1/5 that in the nongettered wafer. At 900°C, the concentration in the gettered wafer drops to 1/2 and, for the long-term gettered wafer, to 1/3. This difference is due to gettering. The Fe concentration after quenching from 1150°C is $3.5 \times 10^{14} \text{ cm}^{-3}$ and corresponds to the solid solubility at

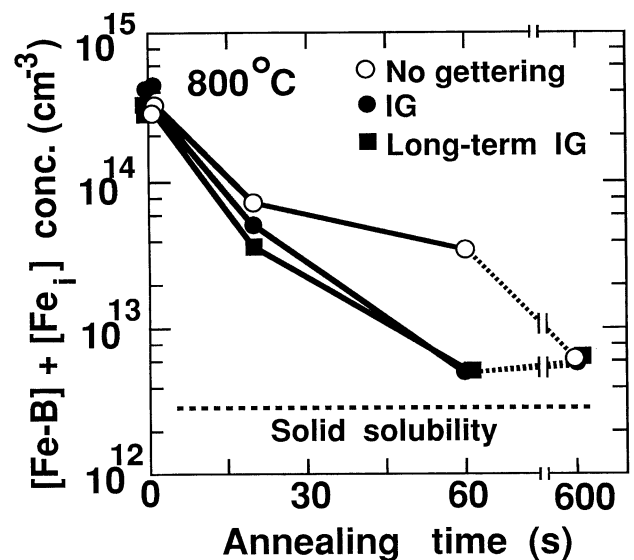


Fig. 5. Dependence of Fe concentration on annealing time at 800°C.

1000°C.¹²⁾ The gettering temperature is lower than this solid solubility temperature, meaning that the supersaturation of Fe impurities is necessary for intrinsic gettering.

Figure 5 shows the dependence of the Fe concentration on annealing time at 800°C. The Fe concentration in the gettered and long-term gettered wafers decreases faster than in the nongettered ones at 60 s. This difference is due to gettering. However, after annealing for 20 s, the concentration of all three types of wafers drops to about 1/4 of those quenched from 1150°C. This suggests that the Fe precipitates into the FeSi_2 ,¹³⁾ which is stable at 800°C. This shows that we cannot effectively getter Fe impurities. The reduction of the Fe concentration stops when the concentration in the denuded zone drops to near the solid solubility. The degree of supersaturation is two orders of magnitude.

Figure 6 shows the dependence of Fe concentration on annealing time at 850°C. The Fe concentration in the gettered and long-term gettered wafers decreases faster than in the nongettered wafer even at 20 s, the same as the isothermal annealing at 60 s at 800°C. The concentration in the nongettered wafer also drops to 1/4 of those quenched from 1150°C. This is due to the precipitation of Fe. Gettering stops when the Fe concentration drops to the solid solubility limit.

The Fe concentration is strongly dependent on the annealing time at 900°C, as shown in Fig. 7. Unlike at 800 and 850°C, the Fe concentration in the nongettered wafer after 30 s of annealing is almost the same as samples quenched from 1150°C, indicating no Fe precipitation into the FeSi_2 phase. In contrast, the Fe concentration in the gettered wafer drops to 1/6 that in the nongettered wafer, so the optimum degree of supersaturation for gettering is one order of magnitude. Iron takes 2.6 s to diffuse through the 20- μm denuded zone.¹²⁾ The effective gettering time is 20 to 30 s (Fig. 7), or about 10 times longer than that required for Fe to diffuse to the defect region. This suggests that gettering is limited by the reaction of Fe with the oxygen precipitates in the

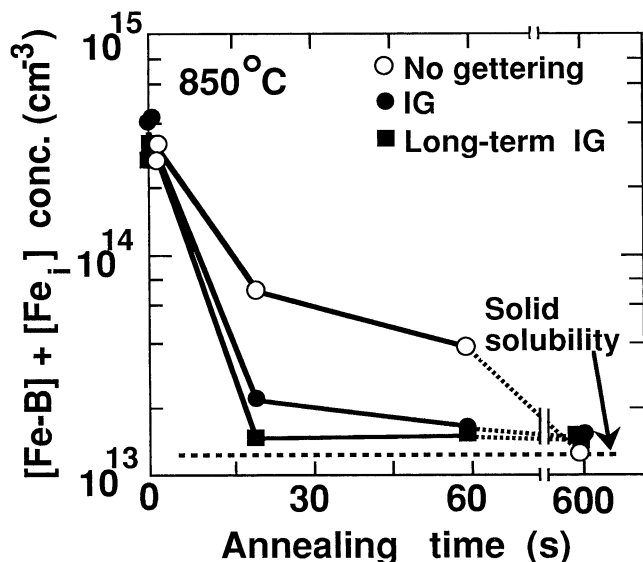


Fig. 6. Dependence of Fe concentration on annealing time at 850°C.

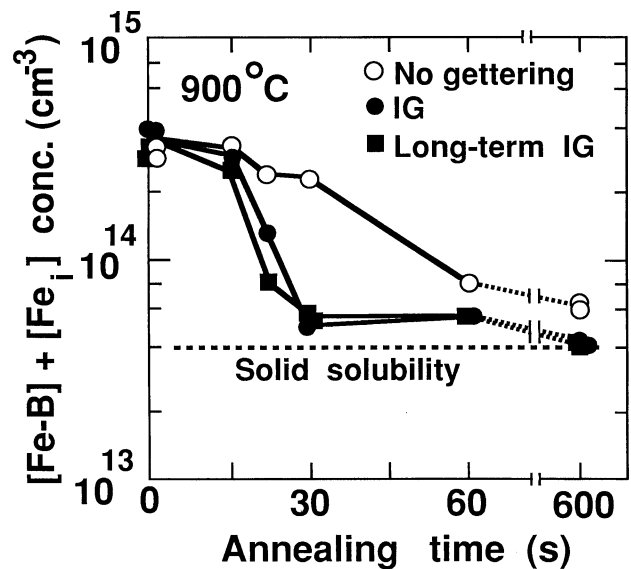


Fig. 7. Dependence of Fe concentration on annealing time at 900°C.

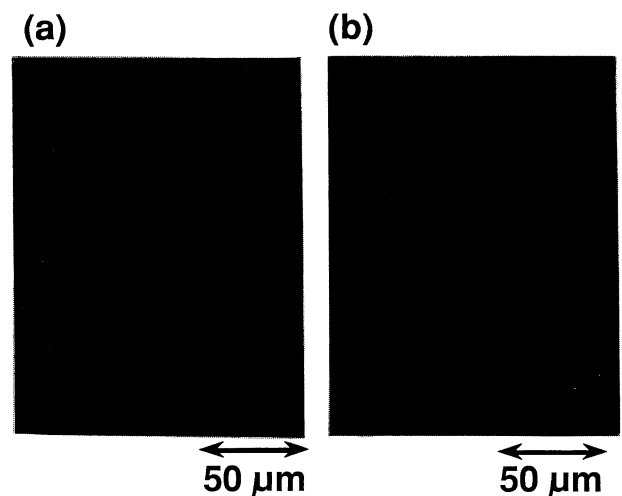


Fig. 8. Optical microscopic images of surfaces after Secco etching for 2 min: (a) nongettered and (b) gettered.

defect region, rather than by Fe diffusion.

Figures 8(a) and 8(b) show images of the surface microdefects observed by Secco etching in a nongettered wafer and a gettered wafer annealed at 900°C for 10 min. Surface microdefects caused by Fe contamination were observed as shallow pits in the nongettered wafer, as shown in Fig. 8(a), but could not be observed in the gettered wafer, as shown in Fig. 8(b). This confirms that Fe concentration in intrinsic gettered wafers drops due to gettering, but that the reduction of Fe in the nongettered wafers is due to precipitation into the FeSi_2 phase.

§4. Conclusions

We studied the intrinsic gettering process of Fe impurities by measuring the change in the Fe concentration near the surface after annealing followed by quenching. The supersaturation of Fe impurities is necessary for the intrinsic gettering of Fe. However, for a higher super-

saturation, Fe impurities precipitate faster than gettering. The optimum degree of supersaturation is one order of magnitude. Gettering is limited by Fe reacting with the oxygen precipitates. Thus, it is possible to further improve gettering efficiency by controlling the wafer cooling rate.

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