

Phosphorus Gettering of Iron in Silicon

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Lifetime change of intentionally Fe-contaminated wafers by phosphorus diffusion gettering was measured by surface photovoltage technique. Two competing phenomena were observed. One was a reduction of Fe content to the solid solubility limit. The other was a reduction by gettering of iron to phosphorus diffusion region. It was found that the gettering efficiency at low temperature was higher than one at high temperature, if phosphorus content is same. A new concept of gettering mechanism is proposed.

1. INTRODUCTION

With increasing degree of integration and complexity of silicon ICs, contamination control becomes a dominant issue for the yield improvement. Phosphorus diffusion gettering (PDG) has been used widely in IC manufacturing. The gettering model of heavy metals in silicon at high temperatures was previously developed by a shift of Fermi-level with increasing phosphorus concentration¹⁻³⁾. It is well known, however, that arsenic diffusion dose not give rise to effective gettering⁴⁾. The Fermi-level effect alone cannot explain the fact. Effective gettering is obtained by the co-operation of the Fermi-level effect and ion-pairing of phosphorus and the substitutional species⁵⁾. On the other hand, in a model reported by Schroter⁶⁾, gettering is attributed to the coupling between local currents of silicon self-interstitials and transition elements. It is suggested that the gettering efficiency is higher at high temperature diffusion rather than at low temperature, though the mechanism is not so clear.

The purpose of this work is to reveal

quantitatively the capability of PDG for Fe, when the process temperature becomes low, and to make the mechanism clear.

2. EXPERIMENTAL

P-type, (100) CZ-Si wafers were used for this experiment. The wafers were intentionally contaminated by dipping them in the 0.1 N HNO₃ solution containing 0.01 to 100 ppm of Fe and spin-drying them. Fe surface concentration was analyzed by VPD method⁷⁾. After contamination, Fe was diffused into the wafers for 60 min at 1000 °C in N₂ ambient. POCl₃ diffusion in N₂ + O₂ ambient, and N₂ annealing for 190, 100 and 60 min at 800, 900 and 1000 °C, respectively, followed Fe diffusion. The process time is normalized by Fe diffusion length at each temperature.

Minority-carrier diffusion length was measured by surface photovoltage (SPV) equipment^{8,9)} (CMS-III, Semiconductor Diagnostics Inc., Woburn, MA). Before the SPV measurement, the surface layer was etched off more than 40 µm thick from each side of the wafer using a chemical solution consisting of 4HNO₃ + HF + CH₃COOH and was treated in buffered HF. The depth profiles of phosphorus and Fe

were analyzed by SIMS.

3.RESULTS AND DISCUSSION

Many researchers have reported the gettering efficiency by detecting amount of gettered species. In this experiment, the efficiency is discussed by measuring lifetime change which is attributed to Fe remaining in the bulk before and after the gettering.

Minority-carrier recombination lifetime (τ) depended on Fe concentration (N_{Fe}) in the bulk as shown in Fig.1. N_{Fe} was estimated from Fe surface concentration. Linear correlation of τ and $1/N_{Fe}$ was obtained in the range of 3×10^{12} to 2×10^{14} Fe/cm³. Abe et al.¹⁰⁾ reported that the relationship of $\tau = 2.5 \times 10^{13} / N_{FeB}$ between recombination lifetime by photoconductivity decay and FeB pair concentration by DLTS. Our data were in good agreement with theirs.

On the other hand, lifetime saturated in low and high Fe contamination level. As shown in Fig.1, when the Fe diffused wafer was annealed at 800 and 900 °C in N₂ ambient, recombination lifetime became longer than that of the as-diffused wafer in case of high Fe contamination level. The lifetime saturated when Fe concentration exceeded 6×10^{12} , 2×10^{13} and 2×10^{14} Fe/cm³ at 800, 900 and 1000 °C, respectively. These values agree with

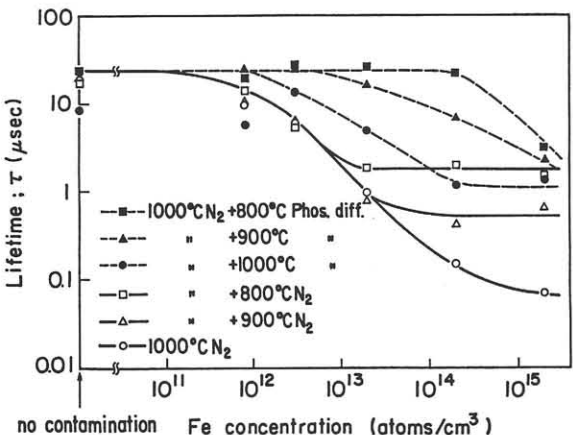


Fig.1 Relationship of recombination lifetime to Fe concentration after Fe diffusion, N₂ annealing and phosphorus diffusion gettering.

the solid solubility limits¹¹⁾ of Fe in Si at each temperature. The formation of FeB pair after annealing has been reported by Graff¹²⁾. These suggest that Fe diffused in the wafer exists as FeB pair at a room temperature. Its concentration is the solid solubility limit at the process temperature. On the other hand, the saturation in the low Fe concentration might be resulted from oxygen or unexpected contamination.

Figure 1 also indicated that PDG at low temperature gave longer lifetime than one at high temperature. Temperature dependence of $1/\tau$ after PDG is summarized in Fig.2. With decreasing of the PDG temperature, the change of $1/\tau$ indicates that Fe concentration remained in bulk became smaller and the gettering efficiency increased.

Depth profiles of phosphorus and Fe after PDG are shown in Fig.3. Fe was gettered to the region where phosphorus concentration exceeded solubility limit¹³⁾. Fe content was larger for high temperature PDG than for low temperature PDG. In spite of constant Fe contamination, the gettering efficiency determined by SPV is different from that by SIMS.

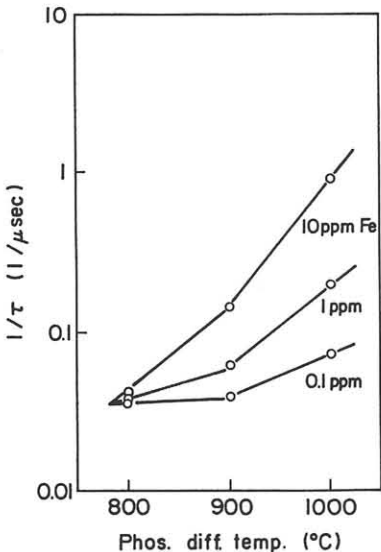


Fig.2 Dependence of a reciprocal of lifetime on phosphorus diffusion temperature.

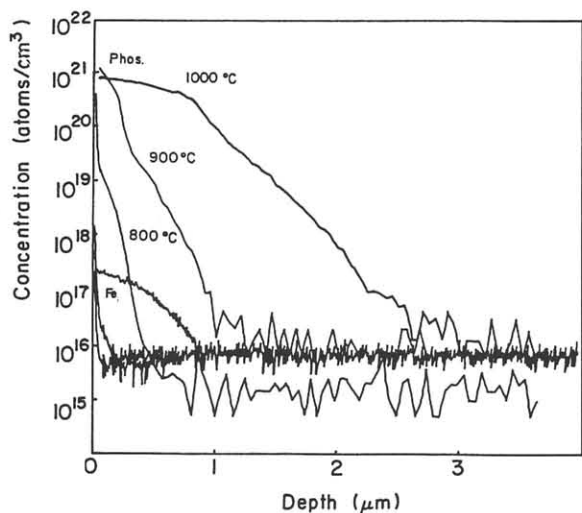


Fig.3 Depth profiles of Phosphorus and Fe concentration after phosphorus diffusion gettering.

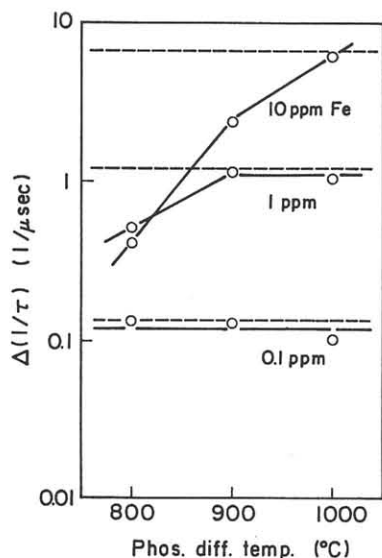


Fig.4 Gettering efficiency taking the solid solubility limit into consideration.

PDG efficiency, which is defined by subtracting $1/\tau$ after PDG from $1/\tau$ which corresponds to Fe solubility limit at each temperature, is shown in Fig.4. Gettering efficiency increased with the temperature of PDG when Fe contamination level is high. This agreed with the results by SIMS as shown in Fig.3. However, this efficiency is determined by the different contamination level, which are resulted from the solubility limit at each temperature. This is not substantial efficiency of PDG.

As shown in Figs.1 and 2, recombination lifetime was longer at low temperature PDG

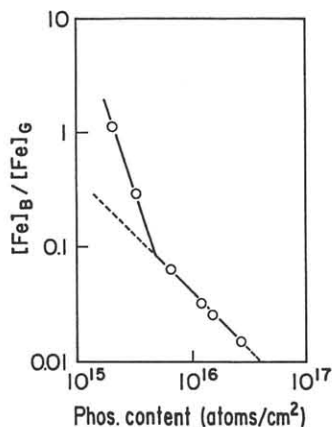


Fig.5 The changes of Recombination lifetime and phosphorus content to phosphorus diffusion time.

than at high temperature. The phenomenon that remains lower Fe concentration at low temperature PDG can be discussed by an equilibrium of Fe between in the gettering site and in the bulk. Figure 5 shows time dependences of recombination lifetime and phosphorus content at 900 °C PDG. Fe contamination level was below the solubility limit at 900 °C in order to obtain only PDG efficiency. The lifetime became longer toward the uncontamination level with increase of the diffusion time. Phosphorus content, which is obtained by integrating the SIMS profile, increased linearly with a square root of PDG time. Fe content remaining in the bulk and gettered Fe content after PDG was calculated. They are expressed by $[Fe]_B$ and $[Fe]_G$, respectively.

Figure 6 plots $[Fe]_B/[Fe]_G$ ratio to phosphorus content (Q_p) in the PDG at 900 °C. $[Fe]_B/[Fe]_G$ ratio became small with increase of phosphorus content. It is found that residual Fe concentration became lower and the gettering efficiency increased. The equilibrium of Fe between in the high concentration phosphorus layer and in the bulk is shown as follows.

$$[Fe]_B/[Fe]_G = K(T)/Q_p \quad (1)$$

$K(T)$ is an equilibrium coefficient and it depends on temperature. In this figure,

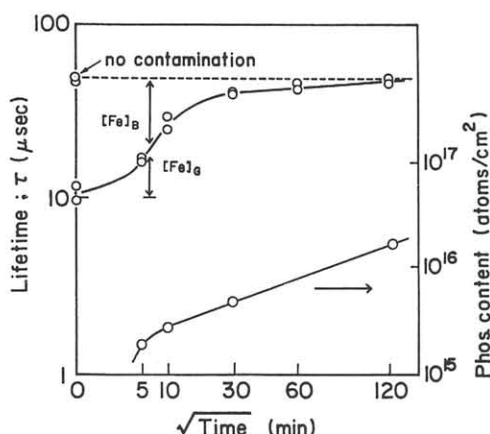


Fig.6 $[Fe]_B/[Fe]_G$ ratio to phosphorus content at 900 °C phosphorus diffusion.

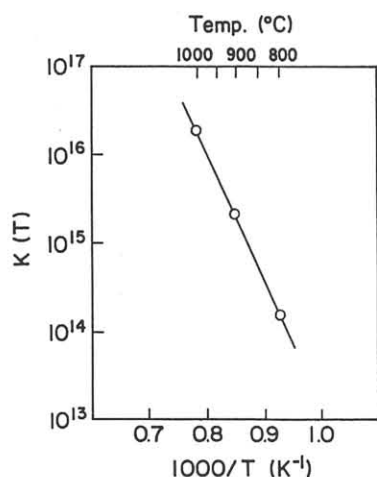


Fig.7 The dependence of equilibrium coefficients on phosphorus diffusion temperature.

deviation of short phosphorus diffusion is caused by a small Fe diffusion length for a short time of PDG.

The dependence of the equilibrium coefficient on PDG temperature is shown in Fig.7. It was indicated that the gettering efficiency at lower temperature was higher than one at high temperature, if phosphorus content is same. The decreased gettering efficiency at high temperature for PDG can not be explained by the silicon interstitial model. The enhanced metal solubility model by the Fermi-level effect and ion-pairing has been developed assuming the capture process to be the rate-limiting step. The equation (1) means the capture process into the phosphorus

diffusion layer and the release process into the bulk play a significant role in limiting the gettering process. The capture process is a rate-limiting step at low temperature. Dominant factor of increase of $K(T)$ at high temperature is the release process. Both steps governs the gettering.

4. CONCLUSION

Phosphorus diffusion gettering of Fe in silicon is discussed quantitatively by new model consisted of the two step reduction of Fe content to the solid solubility limit and the equilibrium between in phosphorus diffusion region and in the bulk of silicon.

The capture and release process governs the gettering, so that, there is an optimum temperature for effective PDG.

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