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Highly Efficient Gettering of Heavy Metals Using Carbon Implanted Eptaxial Si Wafers

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1. Introduction

As the integration scale of LSIs improves, the process temperature is becoming lower to ensure precise dopant distribution. In the gigabit scale device fabrication processes, the maximum temperature is anticipated to be less than 1000 ℃. In addition, epitaxial wafer is becoming to be widely used to obtain highly reliable thin gate dielectrics.[1),2)] However, these trends lead to the reduction of the gettering ability of Si wafers. The reduction of the process temperature reduces number of oxygen precipitates which act as gettering site in the Si wafer. Furthermore, in the case of epitaxial wafers, the density of grown-in defects decreases during epitaxial growth, leading again to the reduction of oxide precipitates. Thus, it is becoming necessary to develop effective gettering technique for future ULSI fabrication. Furthermore, development of method to evaluate the gettering efficiency in a Si wafers is an urgent task.

From these backgrounds, we developed a new method to determine the gettering efficiency of Si wafers. The efficiency is evaluated by measuring the concentration of metal atoms at the wafer surface by TXRF (Total X-ray Reflection Fluorescence) after they were deposited on the back side of the wafer and were diffused by annealing. The effectiveness of the method was confirmed by comparing the results obtained from as received and IG (Intrinsic Gettering) Si wafers. To improve the gettering efficiency of epitaxial wafers, we investigated the extrinsic gettering effect caused by C^+ ion implantation in prior to epitaxial growth, and clarified that C implantation is very effective for heavy metal gettering.

2. Experiment

The Si wafers we used were (100) 4° off Czochralski (CZ)-grown boron-doped wafers, having a specific resistivity of 9-12 Ω•cm and an oxygen concentration of 9×10^{17} /cm^3. These wafers were annealed at 700 ℃, 4 h and 950 ℃, 15 h for IG treatment (IG wafer). The concentration of precipitated oxygen is 2×10^{17}/cm^3. Carbon implanted epitaxial wafers were prepared as follows. Carbon ions were implanted at 60 keV (projected rangeÅ 190 nm) with dose of 1×10^{14}-1×10^{16} / cm^2. In addition to the C implantation, F ion was also implanted (60 keV, 1×10^{15} / cm^2). After the implantation, epitaxial layer (1μm) was grown by using SiH_4 as a source gas at 970 ℃. The defect density in the epitaxial layer was evaluated using OSDA (Optical Shallow Defect Analyzer).[3)] Using these samples, we investigated the gettering efficiency of the wafers for transition and noble metals. The metals we chose were Fe, Ni, Cu and Pt. First, these wafers were dipped in metal dissolved alkaline or HF aqua solution to deposit metals onto the wafer surfaces. The metals were deposited only on the back side surface. Composition and metal concentration in solutions are shown in Fig. 1. Concentrations of metals deposited on the back surface measured using TXRF (Technos TREX 610T) are also shown in the figure. After the depositions, the Fe and Ni deposited wafers went through two step annealing. The first step was 1000 ℃, 1h and the second step was 600 ℃, 1-16 h both in N_2 ambient. Cu and Pt deposited wafers are annealed in N_2 ambient at 900 ℃, 10 min. The metal concentrations at the front surfaces are measured also using TXRF to determine the gettering efficiency.

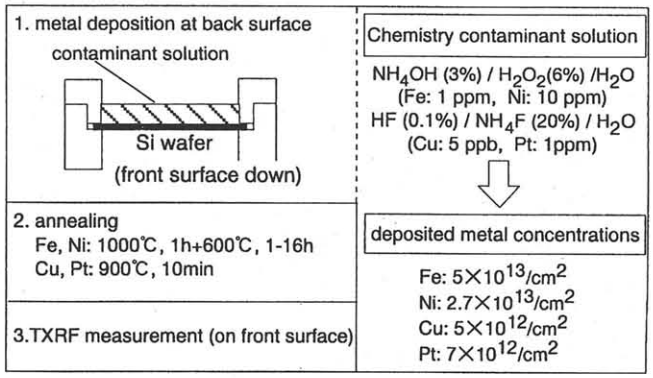

Fig. 1 Experimental procedure to determine the gettering efficiency in Si wafers.

3. Results and discussions

3.1 Evaluation of Gettering Efficiency

The second step annealing (600 ℃) time dependence of Fe and Ni concentrations at the wafer surface is shown in Fig. 2. The results obtained from as received CZ wafers and IG wafers are shown in the figure. In the case of as received wafers, concentrations of Fe and Ni atoms increased with annealing time. After the 1000 ℃ (the 1st step) annealing, almost all the Fe and Ni atoms diffused into the Si wafers with the concentrations lower than their solubility (diffusion lengths of Fe and Ni atoms are much larger than the wafer thickness under this condition). In the 600 ℃ (the 2nd step) annealing, the solubility for Fe atom becomes lower than the current concentration of Fe atoms. This makes the excess Fe atoms near the surface precipitates on the surface and the Fe atoms are depleted near the surface region. So, Fe atoms inside the wafer could diffuse to near surface region and precipitate at the surface during 600 ℃ annealing. This makes the concentration increase with 600 ℃ annealing time. The same phenomenon can take place in the case of Ni atoms. However, since the solubility of Ni atoms is three orders of magnitude higher than that of Fe atoms at 600 ℃, the concentration of Ni atoms are less affected.

In the case of IG wafers, the metal precipitation at the surfaces could occur in the first stage of 600 ℃ annealing. However, metals inside the wafers are gettered by oxide precipitates at the same time. Thus the concentration of metal atoms inside the Si crystals is decreased to the level below the solubility at 600 ℃. Then, the reverse diffusion from the surface to the inside of Si wafers occurs. This caused the decrease in the surface concentrations of metal atoms with annealing time.

In this manner, we could observe the gettering behavior of Si wafers and can conclude that the method we adopted in this work is suitable for evaluating gettering ability.

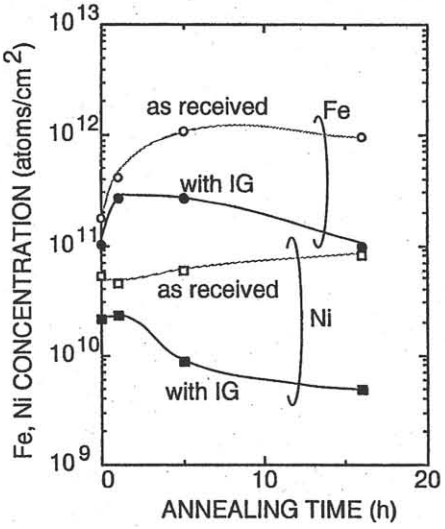

Fig. 2 Fe, Ni concentration at the front surface of as received and IG wafers after second step annealing.

3.1 Gettering Effects in C$^+$ Implanted Epitaxial Wafers

Figure 3 shows the C$^+$ ion implantation dose dependence of the surface metal concentrations. Annealing conditions are also shown in the figure. Concentrations of Fe and Ni atoms decreased as C$^+$ dose increased and their concentrations decreased to below the detection limits of TXRF (5×10^{10}/cm^2 for Fe and 1×10^{10}/cm^2 for Ni) with the dose of higher than 1×10^{14}/cm^2. In the case of Cu and Pt, the surface concentrations didn't change at the implanted dose of 1×10^{14}/cm^2. When the dose exceeded 1×10^{15}/cm^2, their concentrations decreased and concentration of Pt atoms fell below the detection limit. In the case of Cu, the concentrations are about 2.5×10^{11}/cm^2 and 2×10^{10}/cm^2 with the dose of 1×10^{15}/cm^2 and 1×10^{16}/cm^2, respectively. The numbers of gettered Cu atoms can be calculated from the concentrations (difference of non-implanted and implanted samples). The values are about 7×10^{11}/cm^2 and 9.5×10^{11}/cm^2 with each doses.

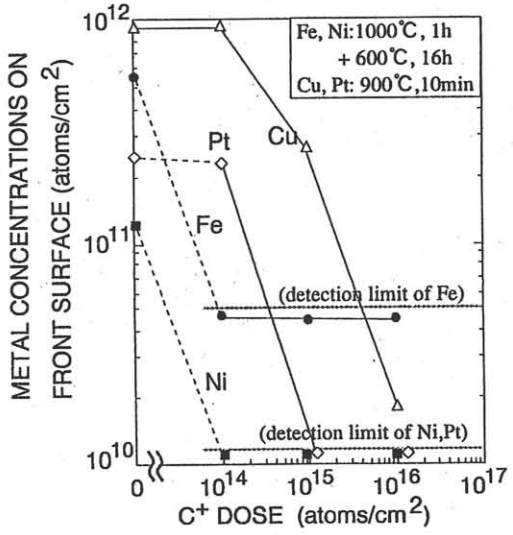

Fig. 3 C$^+$ dose dependence of front surface metal concentrations diffused from back surface.

From these results, it is clarified that the gettering efficiency of the C implanted wafers increase with C$^+$ implanted dose and C implantation is effective to getter of Fe, Ni, Cu and Pt atoms. We also confirmed that the same gettering effects can be obtained by using FZ (Floating Zone) wafer. The result suggests that, the gettering effect is brought out not only by oxide precipitates. The phenomenon can be explained if we assume the Si-C cluster formation in the C implanted region. [4] The cluster is thought to generate stress field around the region, which could getter metal atoms.

Fig. 4 shows the results of defect density measurements in epitaxial layer measured by using OSDA. The density increased with C dose and the value exceeded one order higher than non-implanted sample with the implanted dose of 1×10^{15}/cm^2. However, as shown in the figure, the density can be decreased by adding F ion implantation.

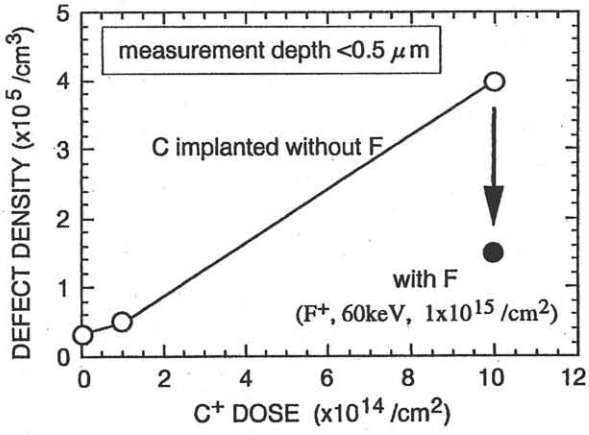

Fig. 4 C$^+$ dose dependence of defect density measured by OSDA.

4. Conclusions

We developed a new technique to determine the gettering efficiency of transition and noble metals in Si wafers. TXRF is utilized to measure the metal concentration at the front surface after the back side contamination and annealing. The effectiveness of the method was confirmed by comparing the result obtained from as received wafers and IG wafers. Furthermore, we applied the method to evaluate the efficiency of C implantation into CZ wafers in prior to epitaxial growth, and clarified that this greatly improve the gettering ability.

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