

Effect of Metals (Fe,Cu) on 8-nm-Thick Gate Oxide Reliability

Yoshimi SHIRAMIZU, Masaru TANAKA, Shinya YAMASAKI, Masaharu NAKAMORI,
Nahomi AOTO and Hiroshi KITAJIMA

*ULSI Device Development Laboratories, NEC Corporation,
1120 Shimokuzawa, Sagamihara, Kanagawa 229 Japan.*

An investigation of the correlation between low-concentration transition metals on the reliability of 8-nm-thick gate oxide found that the critical contamination levels were 4×10^{10} and 3×10^{11} atoms/cm² for iron and copper, respectively. The effect of copper contamination on gate oxide reliability was less serious than of iron, because copper atoms are located at the SiO₂/Si interface while iron atoms are located in SiO₂ films.

1. Introduction

There have been several reports on the dielectric breakdown degradation of gate oxide films caused by metals[1][2]. However, the surface metal concentrations in those reports were more than 1×10^{12} atoms/cm², which is far higher than the contamination level in real silicon processes. To date, gate oxide films of devices under development have been thinner than 10 nm. Therefore, it is important to clarify the effect of metal contamination at these gate oxide thickness. For gate oxide films thinner than 10 nm, the effect of wet cleaning residues (mixture of Al, Ca and Mg) on time dependent dielectric breakdown (TDDB) characteristics has been reported[3]. It is well known that transition metals such as iron have a greater effect on gate oxide degradation than other metals.

In this paper, we report on the correlation between low concentrations of transition metals (Fe and Cu) and the degradation of the reliability of 8-nm-thick gate. We selected iron because of its serious effect on gate oxide reliability and selected copper because copper contamination easily arises from equipment and the cleanroom environment.

2. Experiment

B-doped ($\sim 15 \Omega \text{ cm} <100>$) silicon substrates were intentionally contaminated with iron or copper just before gate oxidation. The concentration of each metal ranged from 1×10^{10} to 1×10^{12} atoms/cm² on silicon

substrate surfaces. In order to control the concentration of surface metals, silicon substrates were pre-oxidized (sacrificial oxidation), the oxides were removed, and then the wafers were dipped into chemical solutions having controlled pH levels (pH=3~9) and including either iron or copper. The pH levels were adjusted using ammonia and nitric acid. The removal of sacrificial oxides was necessary to decrease the background level of metal contamination to below 1×10^9 atoms/cm². The pH control was also necessary to control the surface concentration of the selected metal. Metal concentrations were quantified using Vapor Phase Decomposition - Atomic Absorption Spectrometry (VPD-AAS). The presence of metals in SiO₂ and bulk crystal was evaluated using Secondary Ion Mass Spectroscopy (SIMS).

The reliability of thin gate oxide was tested by measuring the gate oxide breakdown voltage using 1-mm²-area MOS capacitors and TDDB characteristics using 0.1-mm²-area MOS capacitors.

3. Results and discussion

3-1 Metals contamination levels

The amounts of metal (Fe and Cu) contaminants, ranging from about 1×10^{10} to 1×10^{12} atoms/cm² on silicon substrate surfaces, were directly proportional to the amounts of metals (Fe and Cu) in the pH controlled (pH3~9) chemical solutions, as shown in Figure 1. The contamination levels of unintentional metals, such as copper and aluminum in the iron-contaminated sample and

iron and aluminum in the copper-contaminated sample, were lower than 1×10^9 atoms/cm². The concentration of each metal on silicon surfaces could be controlled by the dipping method.

According to the SIMS profile in Figure 2, almost all iron atoms were located in the upper (~ 4 nm) SiO₂ films.

3-2 Reliability of gate oxide films

Figure 3 shows the breakdown voltage for the gate oxides contaminated with iron or copper. For iron contamination of 5×10^{12} atoms/cm², almost all the samples were degraded and showed B-mode failure ($4 \sim 8$ MV/cm). Taking into account the area dependence of MOS capacitor, the critical contamination level for gate oxide degradation was less than a quarter of the reported value for 30-nm-thick gate oxide [2].

Figures 4 and 5 show the cumulative TDDB failure rate for the thin gate oxide films contaminated with iron and copper, respectively. The cumulative rates of random failure were higher for devices contaminated with iron, ranging from 4×10^{10} to 5×10^{11} atoms/cm² in concentration, than for contamination-free devices ($Fe \leq 1 \times 10^9$ atoms/cm²). This contamination level (4×10^{10} atoms/cm²) is about one order of magnitude lower than the reported level.

4. Discussion

The effect of copper contamination on gate oxide reliability was less serious than that of iron contamination. It has been reported that almost copper atoms diffuse into the silicon substrate during oxidation[2] and are located at the SiO₂/Si interface as copper oxide (Cu₂O) or metallic copper [4].

Iron atoms are located in SiO₂ films as metal oxides after gate oxidation. However, since the formation enthalpy of iron oxide is higher than that of silicon dioxide, a smaller amount of iron is located in SiO₂ films given higher temperature oxidation or post-oxidation annealing. Thinner (<10 nm) oxides are formed using lower temperature oxidation than that for 15 nm or thicker oxides. After thin oxide (<10 nm) formation, a larger amount of iron is present in the oxide films than with high temperature

oxidation. Therefore, for thin oxide formation (corresponding to a lower temperature), the effect of iron contamination is more serious. For copper contamination, the amount of copper atoms at the SiO₂/Si interface may be greater than with lower temperature oxidation.

4. Conclusion

We were able to control the contamination level of selected metals ranging from 1×10^{10} to 1×10^{12} atoms/cm² by pH control of chemical solutions and used this method to investigate the effect of low-concentration iron or copper contamination on the reliability of 8-nm-thick gate oxide. From TDDB characteristics, the critical contamination levels were 4×10^{10} and 3×10^{11} atoms/cm² for iron and copper, respectively. Almost all the iron atoms were located in SiO₂, while almost all copper atoms were located at the SiO₂/Si or in bulk crystal. Metals in gate oxide films are the cause of the reliability deterioration of gate oxide films. Therefore, critical concentrations in 8-nm-thick gate oxide films were both about 1×10^{10} atoms/cm² for iron and copper.

Acknowledgments

We thank Dr. O. Mizuno, Dr. M. Kikuchi, and Dr. K. Ikeda for their encouragement and useful discussions and Mr. T. Hayashi for the SIMS analysis.

References

- [1]M. Morita et al., Ext. Abst. of the Jpn. Soc. of Appl. Phys. and Related Soc., Spring Meeting, Vol.2, p.682, 1991.
- [2]M. Takiyama et al., Proceedings of the 7th international symposium on silicon materials science and technology, 1994.
- [3]H. Uchida et al., IEDM proceedings, p.405, 1990.
- [4]Y. Shiramizu et al., IEICE Trans. Electron., Vol.E76-C, No.4, p.635, 1993.

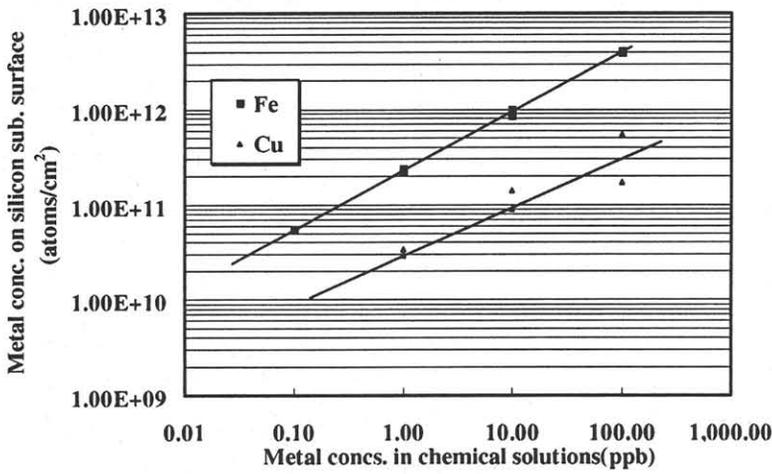


Figure 1 Correlation between Fe and Cu concentration in chemical solutions and Fe and Cu concentrations at the substrate surface.

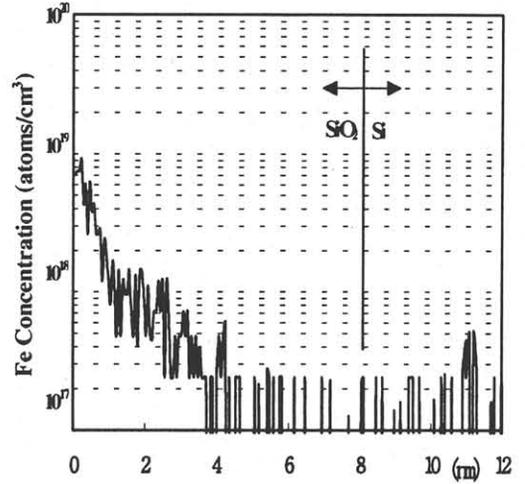


Figure 2 Fe SIMS depth profile in SiO₂ and bulk crystal.

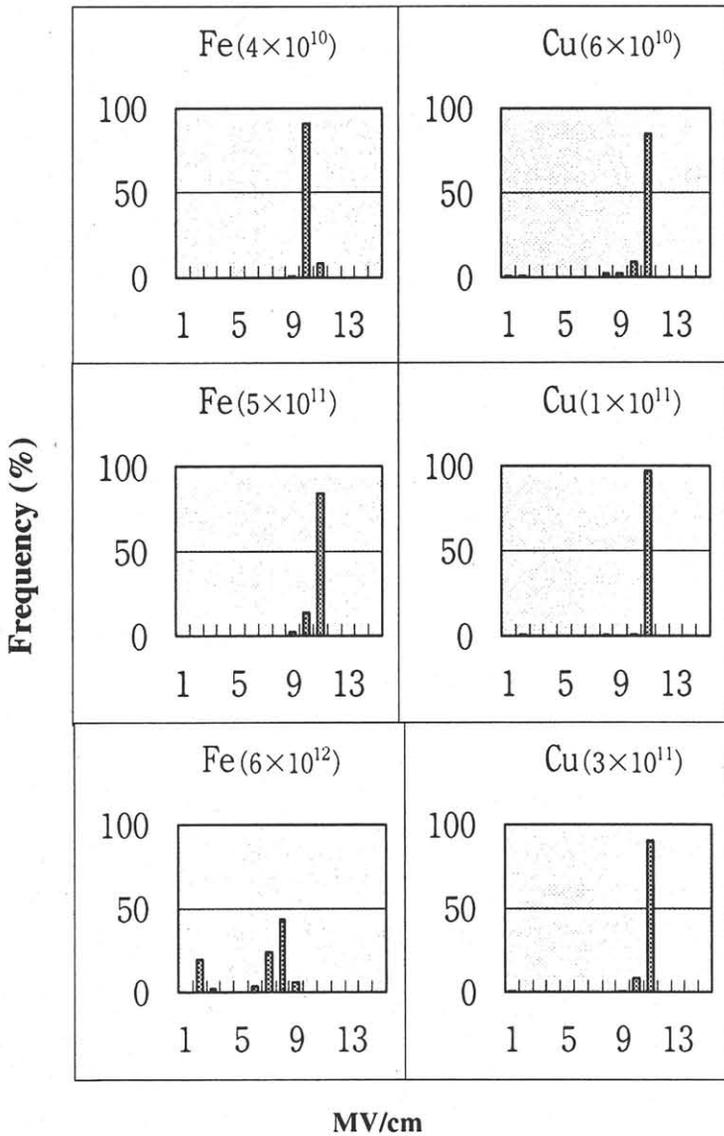


Figure 3 Breakdown voltage of 8-nm-thick gate oxide films contaminated with metals (Fe and Cu).

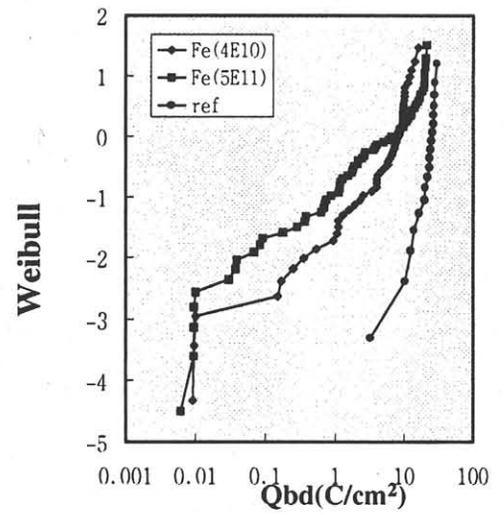


Figure 4 Dependence of TDDB characteristics on Fe concentration on silicon substrate surface.

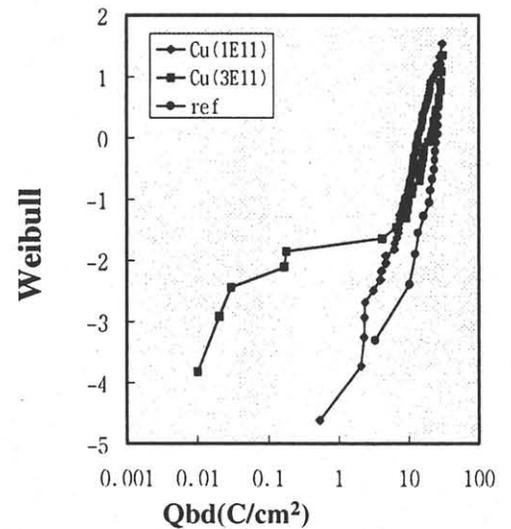


Figure 5 Dependence of TDDB characteristics on Cu concentration on silicon substrate surface.