

## The Oxide Reliability Improvement with Ultra-Dry Unloading in Wet Oxidation Using Load Lock Oxidation System

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We propose a new oxidation method using load lock oxidation system. This enables us to form highly reliable thin oxide. The distinction of this method is to reduce the water concentration ultimately in unloading procedure, combined with wet oxidation method. In this manner, the oxide reliability of both small and big MOS capacitors (intrinsic and extrinsic reliability) is remarkably improved. The method is very promising for future ULSIs, such as flash memories, which require both intrinsic reliability and high uniformity.

### 1. INTRODUCTION

In submicron LSIs, reliability of thin gate oxide is a main concern. For instance, the tunnel oxide in flash memories require high reliability even in a bit operation. On the other hand, the chip size of ULSI memories are becoming larger with integration scale. Therefore, a new oxidation method is demanded which improves both the intrinsic and the extrinsic oxide reliability. One possible method is the ultra-dry oxidation method, as reported in last few years(1)(2). However, this method is not useful to improve the extrinsic oxide reliability. To find a solution to this problem, we controlled moisture of wafer ambient in oxidation and unloading steps in oxidation sequence. Then, we found that the combination of wet oxidation and ultra dry unloading is excellent to form a highly reliable thin oxide.

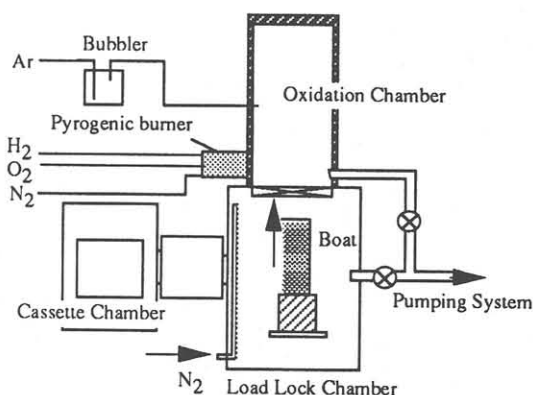


Fig. 1 A schematic of the load lock oxidation system.

### 2. EXPERIMENT

To investigate the oxide reliability dependence on water concentration in each step of the oxidation sequence, we used load lock oxidation system schematically shown in Fig.1. This system allows us to control the wafer ambient moisture in the oxidation step from 3ppb to 50% using bubbler and pyrogenic burner. After the oxidation, the oxidation chamber is evacuated down to less than  $10^{-4}$ Pa. By supplying ultra-dry  $N_2$  and  $H_2O$  from bubbler to oxidation chamber, we can control unloading atmosphere to keep the moisture from 3ppm to 1000ppm. The oxidation sequence adopted in this work is shown in Fig. 2.

Using above oxidation technique, we fabricated MOS capacitors as schematically shown in Fig.3, with 10 nm-thick gate oxide on p-type Si substrate.

TZDB and TDDB measurements were performed to evaluate oxide reliability using sets of MOS capacitors with various capacitor area ( $10^{-6} \sim 0.5 \text{ cm}^2$ ).

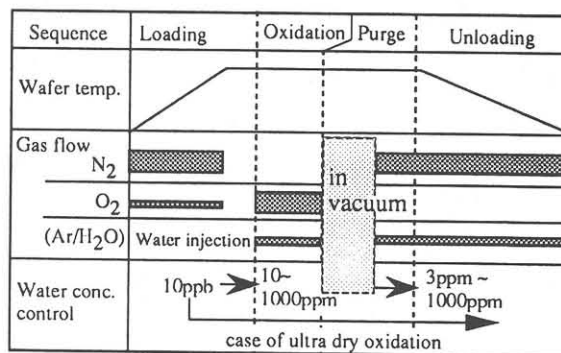


Fig.2 Oxidation sequences in load lock oxidation system.

### 3. RESULTS

Figure 4 shows the distribution of breakdown voltage (gate voltage which causes leakage current of  $10^{-6}\text{A/cm}^2$ ) in TZDB measurement. In this measurement, we used MOS capacitors having  $0.5\text{cm}^2$  gate area (big capacitor) to investigate the extrinsic reliability. It is clearly shown that addition of  $\text{H}_2\text{O}$  in oxidation step improves the extrinsic reliability in the case of ultra-dry unloading condition. On the other hand, even in the case of 1000ppm  $\text{H}_2\text{O}$  in oxidation step, the extrinsic reliability is poor when the unloading condition is wet atmosphere as shown in Fig.5.

Figure 6 shows density of initial defects which cause time-zero breakdown even when the gate voltage is less than 7V. The defect densities decrease with increase of  $\text{H}_2\text{O}$  concentration in oxidation step in the case of ultra-dry unloading.

From these results, it is suggested that the combination of the wet oxidation and dry unloading is suitable to form the gate oxide with excellent extrinsic reliability. Moreover, from the results of the I-V measurement using small capacitors ( $10^{-4}\text{cm}^2$ ), we found that the intrinsic breakdown voltage are also improved with  $\text{H}_2\text{O}$  during the oxidation step as shown in Fig.7.

Figure 8 shows the results of FTIR analysis of gate oxide in the case of ultra-dry unloading condition. The LO peak of Si-O bond shifts to higher wavenumber with increasing  $\text{H}_2\text{O}$  concentration in the oxidation step. This means that even the ppm- $\text{H}_2\text{O}$  in oxidation step have the merit to reduce the oxide film stress that may cause the weakspot formation.

The result can be explained as follows. (1)In the oxidation step,  $\text{H}_2\text{O}$  itself may be a beneficial to oxide reliability. (2)In unloading step,  $\text{H}_2\text{O}$  may cause degradation of oxide reliability by accelerating the growth of poor quality oxide at low temperature, or by increasing  $\text{H}_2\text{O}$  and OH components that remain in the oxide. These assumptions imply us that the oxide reliability may be improved with  $\text{H}_2\text{O}$  in oxidation step and degrade with  $\text{H}_2\text{O}$  in unloading step. As a result, the wet oxidation with ultra-dry unloading should be an excellent method to form a highly reliable thin oxide.

Figure 9 shows the stress electric field dependence of breakdown time in TDDB measurement. In this measurement, we used small capacitors with  $10^{-6}\text{cm}^2$  gate area to investigate intrinsic reliability. In the case of pyrogenic oxidation, which contain 36%  $\text{H}_2\text{O}$ , the intrinsic reliability is remarkably improved for the case of ultra-dry unloading, compared to conventional pyrogenic oxidation method.

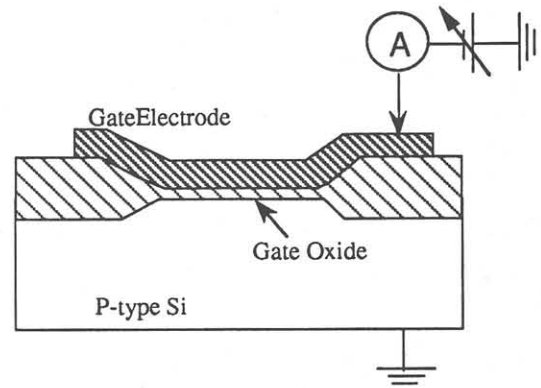


Fig.3 Sample structure

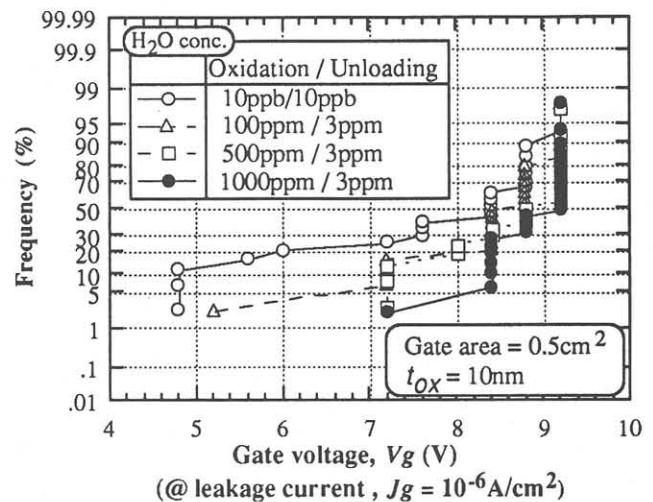


Fig.4 The breakdown voltage of MOS capacitors dependence on  $\text{H}_2\text{O}$  conc. in oxidation step.(Ultra-dry unloading condition.)

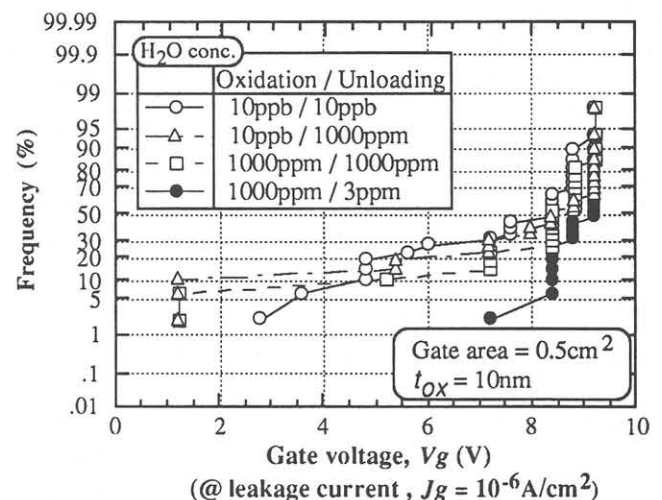


Fig.5 The breakdown voltage of MOS capacitors dependence on  $\text{H}_2\text{O}$  conc. in oxidation and unloading step.

#### 4. CONCLUSIONS

We proposed a new oxidation method using load lock oxidation system that enables us to form the highly reliable thin oxide. The distinction of this method is to reduce the water concentration ultimately in unloading procedure, combined with wet oxidation method. In this way, the oxide reliability was remarkably improved for both small and big MOS capacitors (intrinsic and extrinsic reliability). This oxidation method is very promising for future ULSIs, such as flash memories, which require both ultimate intrinsic reliability and high uniformity.

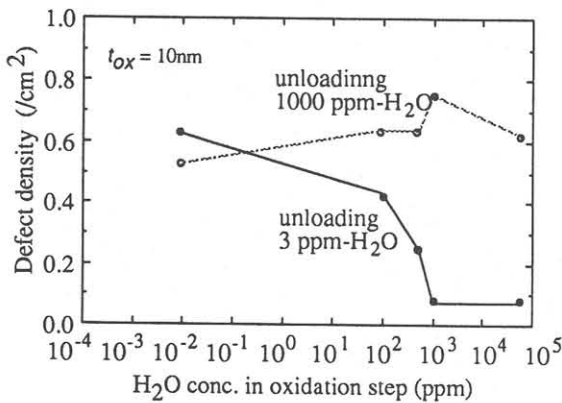


Fig.6 The defect densities dependence on H<sub>2</sub>O conc. in oxidation step.

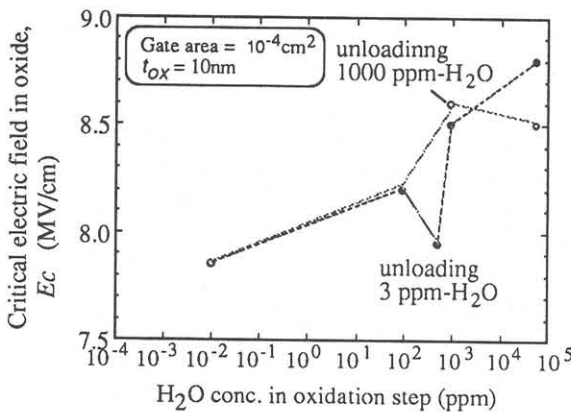


Fig.7 Critical electric field,  $E_c$  dependence on H<sub>2</sub>O conc. in oxidation step. Critical electric field represents the average electric fields in oxide  $E_{ox}$ , when the gate current reach  $10^{-6}$  A/cm<sup>2</sup>. In this study,  $E_{ox}$  is defined as  $(|V_g|-1.1)/t_{ox}$ .

#### ACKNOWLEDGEMENTS

The authors wish to thank Tokuo Kure and Simpei Iijima for their valuable suggestions and encouragement. The authors would also like to thank Takamitsu Nagara for his cooperation in this work.

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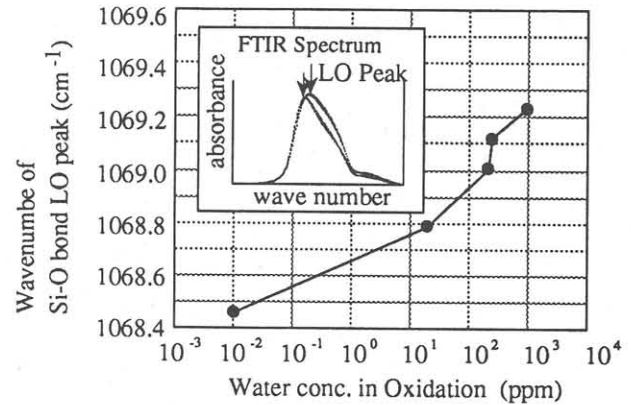


Fig. 8 Wave number of Si-O bond LO peak in FTIR spectrum vs. H<sub>2</sub>O conc. in oxidation step.

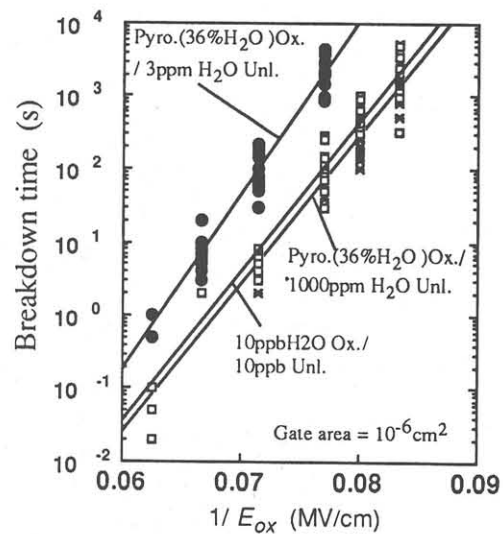


Fig. 9 The breakdown time vs.  $1/E_{ox}$  under constant voltage stress.  $E_{ox}$  represents the average electric fields in the oxide, defined as  $E_{ox} = (|V_g|-1.1)/t_{ox}$ .