Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 258-260

Formation Process of Highly Reliable Ultra-Thin Gate Oxide

K.Ohmi[1)], T. Iwamoto[1)], T.Yabune[1,2)],T.Miyake[1,2)] and T. Ohmi[1)]

1) Department of Electronics, Faculty of Engineering, Tohoku University,
Aramaki Aza-Aoba, Aoba-ku, Sendai, 980-77 Japan
Fax: 022-224-2549, Phone: 022-217-7122
2) Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication,
Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai, 980-77 Japan
Fax: 022-217-5565, Phone: 022-217-5564

A new oxide formation process featuring thermal oxidation in a strongly reductive ambient, called hydrogen-radical-balanced steam oxidation (H^*/H_2O oxidation), followed by post-oxidation annealing has been developed. In this oxidation process, only the strong Si-O bond which is perfectly resistant even to the strongly reductive ambient survives and a high integrity oxide film can be grown. From the results of the breakdown tests by constant current stress (Q_{BD}) and the gate voltage shift (V_g shift) measurement under constant current stress, it has been revealed that the thin oxide film featuring high-integrity in breakdown and strong immunity from electrical stress is obtained by H^*/H_2O oxidation with post-oxidation annealing. This oxidation method is effective to form the thin oxide used under high electric field condition such as a tunnel oxide for flush memories.

1. Introduction

In nonvolatile memories, the thin oxide film is used as a tunneling dielectric to transport electrons to the floating gate[1]. Electrons transportation is carried out under high electric field. That high electric field causes degradation of the dielectric reliability. During transportation of the carriers through the oxide, some of them are trapped. Carrier trapping gives rise to the space charge in the oxide, causing window narrowing and oxide breakdown[2]. In conventional oxidation technologies, when the SiO_2 layer is formed on Si substrates by oxidation of silicon, the mechanical stress and strain are arising at the Si-SiO_2 interface, resulting in imperfections in the Si-O network structure and the formation of local weak Si-O bonds. Once such poor-quality oxides are formed, there is no stage to remove them in conventional oxidation technologies. In order to achieve a low carrier trap density in SiO_2 films, it is necessary to reconsider the oxidation method and/or the oxidation ambient. The purpose of this paper is to propose a new oxide formation process featuring oxidation in a strongly reductive ambient in order to obtain highly reliable ultra-thin oxide based on steam oxidation. This oxide film is formed under the competition between the reduction by active-hydrogen, e.g., hydrogen-radical (H^*) and the oxidation by steam (H_2O). The weak Si-O bonds in the oxide film which are locally formed in oxidation by H_2O are immediately reduced by active-hydrogen. As a result, only the strong Si-O bonds which are perfectly resistant even to the strongly reductive ambient survive and a high integrity oxide film can be grown. We call this oxidation process hydrogen-radial-bananced steam oxidation (H^*/H_2O oxidation).

2. Experimental

In this experiment, MOS capacitors were fabricated with phosphorous-doped polysilicon gate and gate oxides on p-type and n-type (100) substrates. The device isolation was implemented by 600nm field oxide grown at 1000°C in the steam ambient, which was etched by a surfactant-added BHF (HF-NH_4F) solution. The wafers were cleaned in the modified RCA cleaning[3]. The chemical oxides formed in RCA cleaning were removed by diluted HF(0.5%). Then, immediately, the passivation chemical oxides were formed by immersing in ozonized ultrapure water (O_3 concentration was 2ppm) at room temperature (R.T.) for 20 min. We have reported that the passivation chemical oxide is effective to improve gate oxide integrity and reliability[4]. The H^*/H_2O oxidation and dry oxidation were carried out in the same ultraclean oxidation furnace at 900°C by IR lamp[5][6]. The dry oxide was formed in dry O_2 ambient and the H^*/H_2O oxides were formed in $H^*/H_2O/Ar$ ambient.

3. Results and Discussion

Figure 1 shows that the gas distribution system for generation of the $H^*/H_2O/Ar$ gas. A 4m long stainless steel tube having a 20nm thick

Cr_2O_3 film on its inner surface was employed as a gas feed line[7]. The mixture gas of H_2, O_2 and Ar is led to the stainless steel. In the case of the gas feed line heated up to 500°C, hydrogen molecules are completely decomposed to hydrogen radicals (H*) due to the catalytic effect of Ni in the stainless steel. These H* react with oxygen molecules to form H_2O. As a result, the mixture gas of H*/H_2O/Ar is introduced into the furnace. While in the case of the gas feed line kept at R.T., the mixture gas of $H_2/O_2/Ar$ is introduce into the furnace.

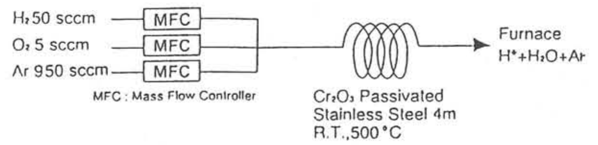

Fig.1 The gas distribution system for generation of the H*/H_2O gas.

Figure 2 shows that the relationship between H_2O generation ratio and the gas feed line temperature or the wafer temperature in the furnace. The H_2O generation ratio is calculated using H_2O concentration measured with Dew Point Meter at the outlet of the furnace. Even in the case of the gas feed line kept at R.T., as a Si wafer is heated up to 600°C, the H_2O generation ratio reaches to 100%.

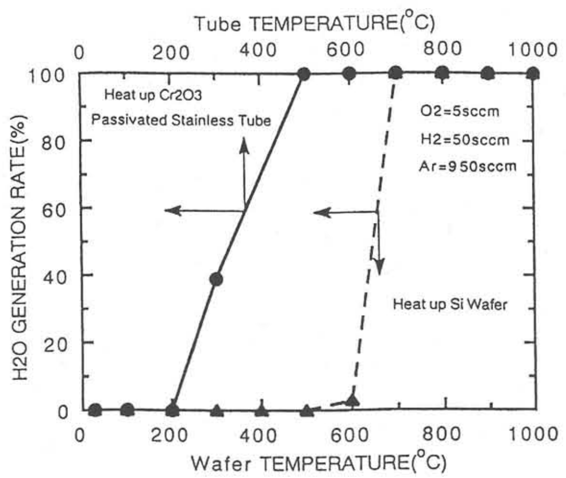

Fig.2 The relationship between H_2O generation ratio and the gas feed line temperature or the wafer temperature in the furnace.

Figure 3 shows that the charge-to-breakdown (Q_{BD}) characteristics of MOS capacitors on p-type substrate under constant current stress (0.1A/cm^2). The oxidations were carried out at 900°C and the post-oxidation annealing was carried out at 900°C for 5 hours in Ar gas ambient. The distributions of the Q_{BD} values of the H*/H_2O oxides are very tight, which results from a high oxide quality. However, the maximum value of Q_{BD} of the H*/H_2O oxide without post-oxidation annealing is lower than that of dry oxide. This result suggests a higher hole trap density for the H*/H_2O oxide without post-oxidation annealing, since the maximum Q_{BD} value is low for a high trap density in oxide films[8]. On the other hand, the distribution of Q_{BD} values is extremely tight, and the maximum Q_{BD} value of H*/H_2O oxide (gas feed line kept at R.T.) with post-oxidation annealing is the highest of the four oxides, which indicate that the hole trap density is reduced by the post-oxidation annealing. Figure 4 shows that the charge-to-breakdown(Q_{BD}) characteristics of MOS capacitors on n-type Si substrate having 7.8nm thick H*/H_2O oxide (gas feed line kept at R.T.) under constant current stress (0.1A/cm^2). The oxidation was carried out at 900°C and the post-oxidation annealing was carried out at 900°C for only 15min in 1%O_2/Ar gas ambient immediately after oxidation. Under substrate injection, the 50% Q_{BD} value is 100.8 C/cm^2 and the maximum Q_{BD} value is 145.8 C/cm^2. This result suggsts that the post-oxidation annealing in 1%O_2/Ar gas ambient is more effective to the chrge-to-breakdown characterics of H*/H_2O oxide than that Ar gas ambient. Figure 5 shows that the dependence of the gate voltage shift of the oxides as a function of the gas feed line temperature under constant current stress(0.1A/cm^2). In the case of the gas feed line heated up, as the temperature of the gas feed line rises, the gate voltage shifts increase. This result indicates that the electron trap density of H*/H_2O oxide (gas feed line kept at R.T.) is extremely low.

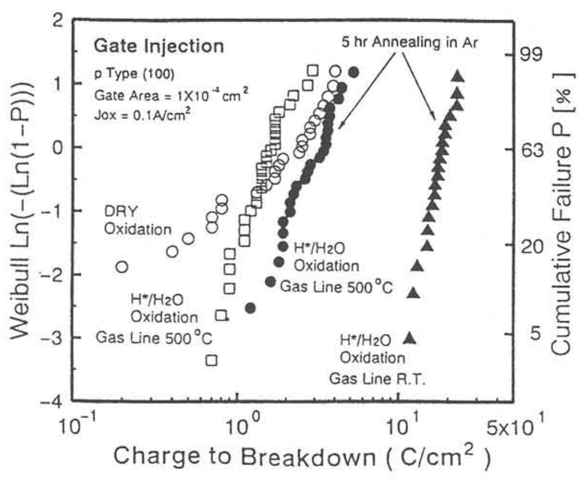

Fig.3 The charge-to-breakdown (Q_{BD}) characteristics (n$^+$-polysilicon/SiO_2/p-Si) under constant current stress (0.1A/cm^2) camparing dry oxide and H*/H_2O oxides with and without post-oxidation annealing. The electrons were injected from the gate to the oxide.

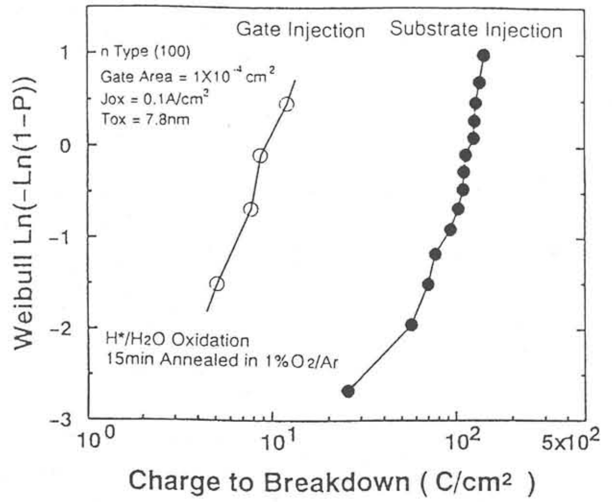

Fig.4 The charge-to-breakdown (Q_{BD}) characteristics of MOS capacitors (n^+-polysilicon/SiO_2/n-Si) having 7.8nm thick oxide under constant current stress ($0.1A/cm^2$). The electrons were injected from the substrate to the oxide.

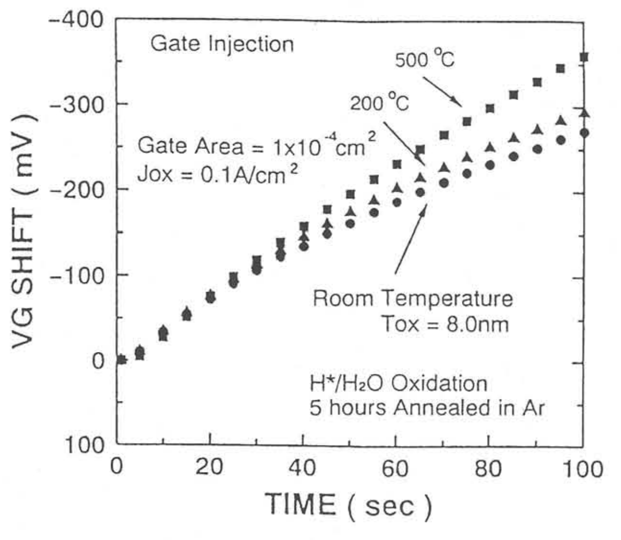

Fig.5 The gate voltage shift of MOS capacitors (n^+-polysilicon/SiO_2/p-Si) as a function of the gas feed line temperature under constant current stress ($0.1A/cm^2$). In the case of the gas feed line kept at R.T., the Vg shift is the smallest, because the electron trap density of this oxide is extremely low.

4.Conclusion

A new oxide formation process featuring thermal oxidation in an strongly reductive ambient, called H^*/H_2O oxidation, followed by post-oxidation annealing has been developed. In this oxidation process, only the strong Si-O bond which is perfectly resistant even to the strongly reductive ambient survives and a high integrity oxide film can be grown. In the case of H^*/H_2O oxidation (gas feed line kept at R.T.) followed by the post-oxidation annealing in Ar gas ambient for 5 hours, the highest quality of H^*/H_2O oxide was obtained. And it was found that the post-oxidation annealing in $1\%O_2/Ar$ gas ambient was more effective to charge-to-breakdown characteristics of the H^*/H_2O oxidation than that in Ar gas ambient. This oxide is a good candidate as thin oxide for high electric field condition uses, such as a tunnel oxide for flush memories.

Acknowledgment

This study was carried out at Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University.

References

[1] A.Bhattacharyya, Solid-State Electron. vol.27, p.899, 1984.
[2] I.C.Chen, S.E.Holland and C.Hu, IEEE Trans. Electron Devices, vol.ED-32, P.413, 1985.
[3] T.Ohmi, M.Miyashita, M.Itano, T.Imaoka and I.Kawanabe, IEEE Trans. Electron Devices, vol.39, P.537,1992.
[4] J.Takano, K.Makihara and T.Ohmi, Mat. Res. Soc. Symp. Proc., vol.315, p.381,1993.
[5] T.Ohmi, M.Morita, A.Teramoto,K.Makihara and K.S.Tseng, Appl. Phys. lett., 60, 2126, 1992.
[6] K.Makihara, A.Teramoto, K.Nakamura, M.Y.Kwon, M.Morita and T.Ohmi, Jpn. J. Appl. Phys., vol.32,p.294, Jan. 1993.
[7] T.Ohmi et al., J.Electrochem, Soc., vol.140, p.1691, 1993.
[8] I.C.Chen, S.Holland, K.K.Young,C.Chang and C.Hu, Appl. Phys. Lett., vol. 49, p.669, 1986.