Extended Abstracts of the 2003 International Conference on Solid State Devices and Materials, Tokyo, 2003, pp. 488-489

P3-20L

A Novel Process for Oxynitride by Post-Oxidation of NH_3 Plasma Nitridation

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Introduction

For lower power consumption, higher speed and circuit stability, multiple-thickness for gate oxide (T_{ox}) is necessary for the system-on-a-chip (SOC) devices [1]. In this study, NH_3 plasma process was used for nitridation of silicon [2], and an ultra-thin nitride layer (~13Å) would be formed after NH_3 plasma treatment. A Novel process was developed for gate oxynitride by post-oxidation on the NH_3 plasma treatment substrate. The reliability was improved by increasing the post-oxidation time, including the less trap densities, better SILC immunity, lower charge trapping and higher Q_{bd}. This novel process makes the multiple T_{ox} possible and easy implements to SOC process integration.

Experiments

Metal/oxide/silicon (MOS) capacitors were fabricated in this work. First of all, the NH_3 plasma nitridation effects were studied. Secondly, rapid thermal (RT) N_2O post-oxidation was performed to compare with O_2 post-oxidation. Finally, A physical model was proposed for the post-oxidation of NH_3 plasma nitridation. The key processes for the NH_3 plasma nitridation were shown in Fig. 1 (a) O_2 and (b) RT N_2O post-oxidation, respectively. The NH_3 plasma was generated by ratio frequency.

Results and Discussion

Physical Model for Post-Oxidation of NH_3 Plasma Nitridation

A physical model for the post-oxidation of NH_3 plasma nitridation was schematic as shown in Fig. 2. The NH_3 plasma processed surface forms a nitride thin film and results in low oxidation growth rate. This process makes the multiple-thickness process possible and easy to implement to SOC process integration.

NH_3 Plasma Nitridation Effects

The NH_3 plasma nitridation effects on gate oxide thickness, nitrogen distribution, and electrical properties were systematic studied. Figure 3 shows the gate oxide thickness for all samples with different plasma exposure time. It can be seen that a significant difference of oxidation growth rate affected by plasma nitridation. The growth rate can be reduced 80% for the sample with NH_3 plasma treated 5 min. This process makes the multiple-thickness-gate-oxides possible. It could be due to the nitrogen-plasma radical (N^*) to form a nitride layer with silicon substrate, and retard the oxidation rate. The SIMS depth profiles of nitrogen, oxygen and aluminum were shown in Fig. 4. The silicon surface was treated by NH_3 plasma and post oxidized in O_2. It shows that the nitrogen accumulated at the Si/SiO_2 interface and broadened into silicon-bulk.

The F-N tunneling current characteristics are shown in Fig. 5. For the thin oxide, it can be seen that a higher leakage current in the low voltage regime. It was due to direct tunneling. The leakage current is low enough for application to DRAM capacitors. The breakdown field is higher as decreasing the thickness as shown in Fig. 6.

The energy released in the thinner oxide was much less due to charge direct tunneling. It shows in Fig. 7, the gate voltage shift, ΔV_g, under a constant current of –10 mA/cm^2 stressing. The gate voltage shift is much smaller, small charge trapping rate, for the NH_3 pretreated sample. The nitrogen incorporation terminated dangling bond in the oxide/silicon interface. The plasma damages were annihilated due to the post oxidation procedures.

Post Rapid Thermal N_2O Oxidation Effects

Figure 8 shows the oxide thickness for samples with and without NH_3 plasma 5 min versus RT N_2O oxidation time. The thickness of sample with plasma 5 min is 13Å. It was similar to the silicon nitride layer, which refractive index was in the range of 1.68~1.99. The nitrogen depth SIMS profile was shown for RT N_2O oxidation sample with and without NH_3 plasma, respectively as shown in Fig. 9. NH_3 plasma process would lead to about one order higher nitrogen concentration compare to the control sample. As shown in Fig. 8, the thickness of plasma samples is 33Å and 36Å with RT N_2O re-oxidation for 30 and 60 sec, respectively. We can conclude that the nitrogen introduced by NH_3 plasma dominated the oxide growth rate rather than RT N_2O re-oxidation.

The oxide breakdown electric field was shown in Fig. 10 for NH_3 plasma samples with RT N_2O processes. It showed that a better oxide reliability for the longer re-oxidation. It was due to the higher nitrogen redistribution and plasma damage removal by the following RT N_2O thermal cycle. It's consistent for the hysteresis characteristics of C-V curves as shown in Fig. 11. The stress-induced-leakage-current (SILC) was shown in Fig. 12 for RT N_2O samples (a) with and (b) without NH_3 plasma nitridation, respectively. The stress condition was -10 mA/cm^2. For the RT N_2O sample with NH_3 plasma nitridation, there was no SILC but for the conventional RT N_2O sample, leakage current increasing. This indicated that the plasma sample has stronger SILC immunity due to the higher nitrogen concentration. Figure 13 shows the gate voltage shift under constant gate injection current, -10 mA/cm^2. Longer the RT N_2O re-oxidation, lower the charge trapping and higher charge to soft-breakdown were.

Conclusions

A novel re-oxidation of NH_3 plasma nitridation process was proposed which obtain different oxide thickness by controlling the NH_3 plasma exposing time. The trap generation rate and bulk trap density was dereasing by increasing NH_3 plasma exposure. The oxide reliability for NH_3 plasma processed sample was improved by increasing the RT N_2O re-oxidation time, including the less bulk trap densities, better SILC immunity, lower charge trapping rate and higher Q_{bd}.

Acknowledgements

This work was supported by the national-science-council of R. O. C. through research contract NSC 91-2215-E-182-004.

References

[1] C. T. Liu, et al., *IEDM Tech.. Dig.*, 1998, pp. 589-592.
[2] Chao Sung Lai, et al., *IEEE Trans. on Electron Devices*, vol.43, 1996.

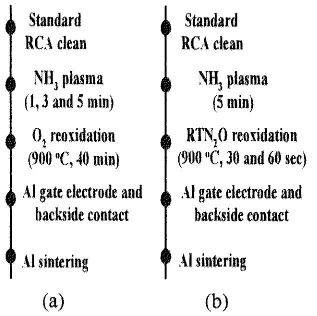

Fig.1. The key processes for the NH_3 plasma nitridation were shown in (a) O_2 and (b) RT N_2O post-oxidation, respectively.

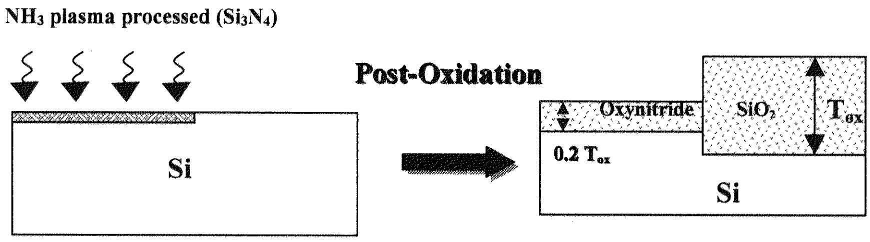

Fig.2. Physical model for the post-oxidation of NH_3 plasma nitridation. The difference of oxide thickness between NH_3 plasma pre-treated oxynitride and SiO_2 films are about 80% .

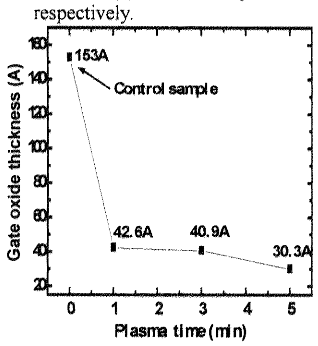

Fig.3. Gate oxide thickness measured by ellipsometer for control sample and NH_3 plasma pretreated samples with exposed time of 1 min, 3 min and 5 min, respectively (NH_3 plasma + O_2 re-oxidation).

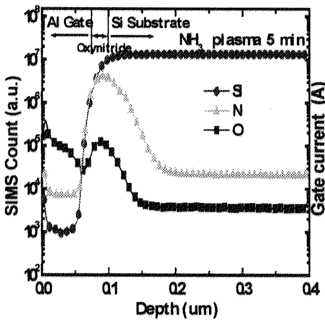

Fig.4. The SIMS depth profile of MOS structure with gate dielectric pre-treated by NH_3 plasma 5 min.

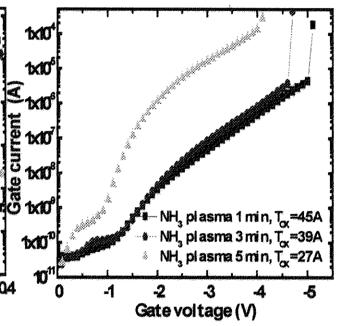

Fig. 5. The characteristic of I-V curves for different plasma exposed time. The oxide thickness was determined by C-V measurement.

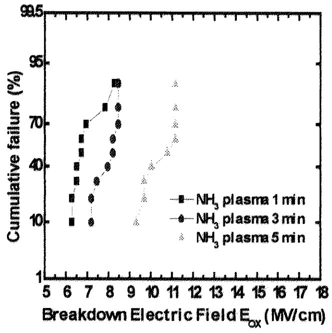

Fig.6. Cumulative plots of breakdown electric field for different NH_3 plasma pre-treated time.

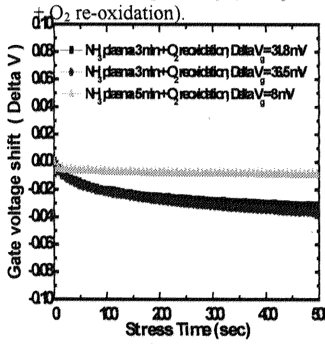

Fig.7. Plot of gate voltage shift under constant current stress at J= $-10mA/cm^2$ for different NH_3 plasma pre-treated time. $\Delta V_g = V_g(t) - V_g(t = 0)$.

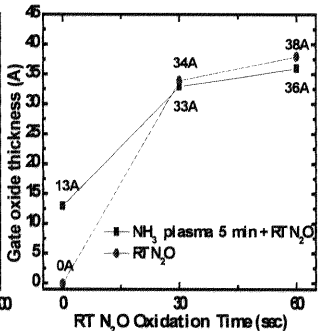

Fig.8. Gate oxide thickness for conventional RT N_2O oxidation and NH_3 plasma pre-treated RT N_2O oxidation as a function of oxidation times.

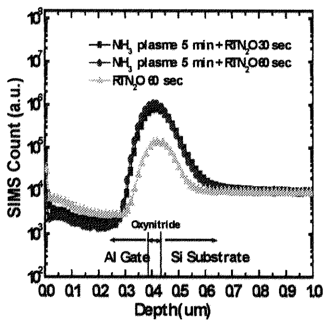

Fig.9. The SIMS depth profile for NH_3 plasma pre-treated and control sample with RT N_2O oxidation.

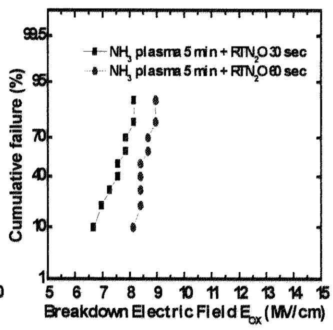

Fig.10. Cumulative plots of breakdown electric field for different RT N_2O re-oxidation time.

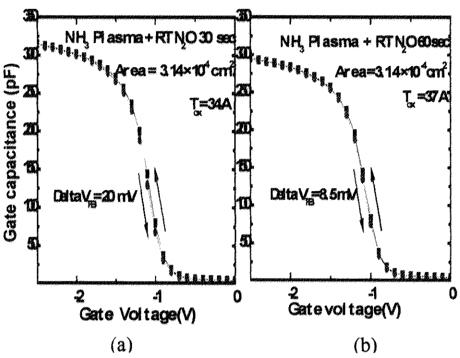

Fig.11. The hysteresis characteristics of high-frequency C-V curves for RT N_2O re-oxidation with NH_3 plasma pre-treated for (a) 30 and (b) 60 sec, respectively.

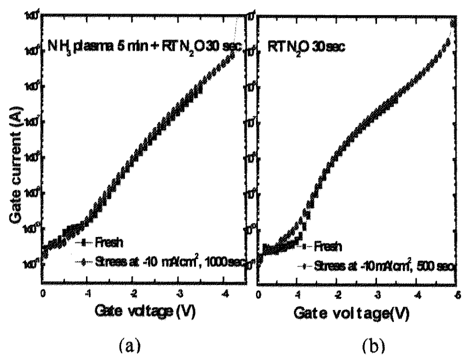

Fig.12. The SILC characteristics for (a) RT N_2O re-oxidation with NH_3 plasma pre-treatment, stressing for 1000 sec and (b) conventional RT N_2O sample, stressing for 500 sec under constant current stress at J_{stress}= $-10\ mA/cm^2$.

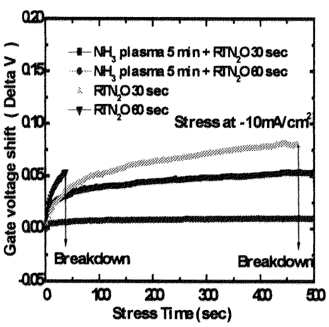

Fig.13. Gate voltage shift under constant current stress at J_{stress}= $-10\ mA/cm^2$ for conventional RT N_2O and RT N_2O re-oxidation with NH_3 plasma pre-treatment.