Ultra-Thin Silicon Oxynitride Film Grown at Low-Temperature by Microwave-Excited High-Density Kr/O₂/N₂ Plasma

Kazuo Ohtsubo, Yuji Saito, Katsuyuki Sekine, Masaki Hiramaya, Shigetoshi Sugawa, Herzl Aharoni^{††} and Tadahiro Ohmi[†]

Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, Aza-Aoba 05, Aramaki, Aoba-ku, Sendai 980-8579, Japan Tel: +81-22-217-7124, Fax: +81-22-263-9395, E-mail: saito@sse.ecei.tohoku.ac.jp *At leave from the Department of Electrical and Computer Engineering, Ben-Gurion University, Beer-Sheva 84105, Israel, Fax: +972-7-6472-949, E-mail: herzl@ee.bgu.ac.il

[†]New Industry Creation Hatchery Center, Tohoku University, Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

1. Introduction

With the trend towards scaling down of metal-oxidesemiconductor(MOS) devices, thinner gate oxide films (< 5 nm) are required for sub-quarter-micron technology. As the gate oxide thickness is reduced below 3 nm, several problems arise such as the increase of gate leakage current and/or boron penetration. This causes degradation of the electrical properties of the MOS devices. To solve these problems, oxynitride (SiON) film is considered to be promising for the replacement of the gate SiO₂ film [1]. The purpose of this paper is to investigate the electrical properties of oxynitride films grown in microwave-excited high-density Kr/O₂/N₂ mixed plasma at 400 °C. Lowering process temperature of gate oxynitride formation process is essential for the realization of ultra-high integration devices featuring precise doping profile control. This technology is used here since it already demonstrated to form high integrity thin SiO₂ films [2]. The preliminary experiments described here demonstrate good quality oxynitride film formation.

2. Experimental

Silicon oxynitride films are grown in Kr/O₂/N₂ mixed plasma employing microwave-excited (2.45 GHz) highdensity plasma system [3] at 400 °C. Four mixing ratios are used. In all of them, the O₂ pressure was 3%. Four partial pressures were used for the N₂ namely 0.5%, 1%, 2% and 5% within the inert gas (Kr). The total pressure in the vacuum chamber was 1 Torr. MOS capacitors [n-type poly-Si/SiON/n-type (100)Si(Cz) $3-5\Omega \cdot cm$] were fabricated. The dopant in both substrate and poly-Si was phosphorus. The results presented below were measured on the above samples.

3. Results and Discussion

Fig. 1 shows Si2p XPS spectrum of silicon oxynitride film grown by the $Kr/O_2/N_2$ plasma. XPS spectrum of the silicon oxide grown by Kr/O_2 plasma is also shown as a reference. The mixing ratios are indicated in Fig. 1 as well. The chemically shifted Si2p peak of the film grown by $Kr/O_2/N_2$ plasma is about 0.3eV lower than that grown by Kr/O_2 plasma. Secondary ion mass spectrometry (SIMS) depth profile of 10nm oxynitride film grown by the $Kr/O_2/N_2$ plasma is shown in Fig. 2. Nitrogen is piled up in the interface of oxynitride and silicon substrate.

Fig. 3 shows Fowler-Northeim (F-N) plot of J-E characteristics of 5 nm oxynitride films. The slope of F-N



Fig.1 XPS spectra of silicon oxide formed by Kr/O_2 and $Kr/O_2/N_2$ plasma



Fig.2 SIMS data of oxynitride film grown by $Kr/O_2/N_2$ plasma





plot decrease and the barrier height (ϕ_b) is lowered as N₂ mixing ratio increases in Kr/O₂/N, plasma.

Figs.4(a)(b) shows charge-to-breakdown (Q_{BD}) and stress induced leakage current (SILC) at 6MV/cm electrical field respectively of 5nm oxynitride films grown by $Kr/O_2/N_2$ plasma with different N_2 mixing ratios. Q_{BD} and SILC of oxide film grown by Kr/O_2 plasma is also shown as a reference. Higher Q_{BD} and lower SILC than that of Kr/O_2 is obtained with the addition of 0.5 % N_2 in $Kr/O_2/N_2$ plasma. On the other hand, both Q_{BD} and SILC are degraded with the addition of 5 % N_2 in $Kr/O_2/N_2$ plasma.

Fig. 5 shows optical emission intensity of oxygen radical O^{*} (777 nm) and nitrogen radical N₂^{*} (316 nm) of the Kr/O₂/N₂ plasma as a function of N₂ mixing ratio (X%). N₂^{*} (391 nm) is not observed in Kr/O₂/N₂ plasma. The intensity of O^{*} (777 nm) decreases and that of N₂^{*} (316 nm) increases with increase of N₂ mixing ratio (X%). From these results, it seems that the oversupply of N₂ in the Kr/O₂/N₂ plasma suppress the amount of O^{*}. This is related to the degradation of the electrical properties mentioned, as the amount of the introduced N₂ is increased.

Fig. 6 shows J-E curve of 3 nm oxynitride films with three N₂ mixing ratios in Kr/O₂/N₂ Plasma. The leakage current of oxynitride film grown in Kr/O₂/N₂ plasma at N₂=0.5 % is slightly lower than that of Kr/O₂ plasma oxide. On the other hand, the leakage current of oxynitride film grown in Kr/O₂/N₂ plasma increases with the addition of N₂ mixing ratio over 1 %.

Fig. 7 shows SILC properties of $Kr/O_2/N_2$ oxynitride, Kr/O_2 oxide and dry thermal oxide. The SILC properties of $Kr/O_2/N_2$ oxynitride (Fig.8(a)) and Kr/O_2 oxide (Fig.8(b)) are almost the same. Each of the J-E curves of Fig. 8 was obtained under constant current stress of 1 A/cm² and 0.5, 1, 2, 5, 10, 20, 50, 100 C/cm². It is noted that while the J-E curve of the thermal oxide (Fig. 8(c)) exhibit higher leakage current with increasing injected charge, the $Kr/O_2/N_2$ and Kr/O_2 J-E curves are almost identical (converged) and do not exhibit such degradation.

4. Conclusion

Highly-robust ultra-thin silicon oxynitride films can be formed at low temperature with the addition of a small amount of N_2 to Kr/O₂ high-density plasma. SILC (5nm) and leakage current (3nm) of oxynitride is decreased with respect to that of oxide film grown by Kr/O₂ plasma with the same oxide thickness. It is thereby demonstrated that this is an effective technology for the formation of ultra-thin gate insulator for giga-scale integration devices.

Acknowledgment

The authors would like to thank ULVAC-PHI, Inc. for the SIMS measurement.

References

- [1] G. Lucovsky et al., JVST A, Vol.17(4), p.1340 (1999)
- [2] M. Hirayama et al., IEDM Tech. Dig., p.249 (1999)
- [3] T. Yamamoto et al., Jpn. J. Appl. Phys., Vol.38, pt.1, No.4A, p.2082 (1999)



Figs.4(a)(b) Charge-to-breakdown (a) and stress induced leakage current (SILC) as a function of the charge injection (substrate injection) (b) of oxynitride films grown by $Kr/O_2/N_2$ plasma of 0%, 0.5% and 5% N₂.



Fig.5 Optical emission intensity of O (777 nm) and N_2 (316 nm) as a function of the N_2 mixing ratio (X%)



Fig.6 J-E curve of 3 nm oxynitride films at three N_2 mixing ratios in Kr/O₂/N₂ plasma



Fig.7 Stress induced leakage current (SILC) of 3 nm gate insulator grown by $Kr/O_2/N_2$, Kr/O_2 and thermal oxidation