# Highly Reliable Oxynitride Gate Dielectrics for Dual Gate CMOS Applications

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Several oxynitride gate dielectrics (NH<sub>3</sub>-nitrided, reoxidized NH<sub>3</sub>-nitrided, N<sub>2</sub>-annealed NH<sub>3</sub>nitrided and N<sub>2</sub>O grown oxides) are investigated and compared for use in p<sup>+</sup>-polysilicon gate MOS devices. The comparison is based on flatband voltage shift as well as decrease in inversion capacitance. Due to the inadequacy of N<sub>2</sub>O and NH<sub>3</sub>-based gate dielectrics to achieve excellent hot-carrier reliability and excellent boron stopping potential simultaneously, a novel technique involving processing in both N<sub>2</sub>O and NH<sub>3</sub> is developed, essential for aggressively scaled dual gate CMOS devices.

## 1. INTRODUCTION

Oxynitride gate dielectrics have received a considerable attention as a substitute for conventional SiO<sub>2</sub> in submicron MOS devices. These dielectrics are attractive for surface channel p+-polysilicon gate p-MOSFETs, due to their improved barrier properties against boron penetration [1-5]. However, there is a trade-off between the barrier properties and hot-carrier reliability of NH<sub>3</sub>-based oxynitride gate dielectrics [3]. Whereas high nitrogen concentration is required to prevent boron penetration, hydrogen incorporation resulting from heavy NH3-nitridation required for this purpose deteriorates hot carrier reliability of these dielectrics. Consequently, N2O-based gate dielectrics are attractive. Although significant work has been presented on the hot-carrier reliability aspects of N2O-based gate dielectrics, relatively less attention has been given to the boron penetration problem [2]. Specifically, a comparison among various NH<sub>3</sub>-based and N<sub>2</sub>O-based gate dielectrics is missing. In this paper, we present a detailed comparison of barrier properties of various NH<sub>3</sub>-based oxynitrides vs. N<sub>2</sub>O-grown oxides. A new technique, which combines N<sub>2</sub>O and NH<sub>3</sub> processing, is demonstrated to realize excellent boron stopping potential as well as excellent hot carrier reliability properties.

### 2. EXPERIMENTAL

Oxynitride gate dielectrics were fabricated by oxide growth in N<sub>2</sub>O ambient, NH<sub>3</sub>-nitridation of O<sub>2</sub>-grown oxides and O<sub>2</sub> or N<sub>2</sub> anneal of NH<sub>3</sub>-nitrided oxides. Ptype substrates with (100) orientation were used. Tables I and II provide a summary of nomenclature used for these dielectrics and the respective processing conditions. After 4000 Å polysilicon deposition, BF<sub>2</sub> implants were performed at 50 keV to a dose of  $5.5 \times 10^{15}$  cm<sup>-2</sup>. Post-implant drive-in was performed in N<sub>2</sub> at various temperatures for 30 min. High frequency and quasistatic C-V measurements were used to characterize the boron penetration.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows normalized inversion capacitance (Cos.inv/Cox) of MOS capacitors with various gate dielectrics. The reduction of inversion capacitance below oxide capacitance (Cox) is caused by depletion of polysilicon under this bias condition, due to insufficiently doped polysilicon gate. The smaller the Cos,inv/Cox ratio, the larger is the polysilicon depletion effect. Thus, NH3 and NH3/N2 samples show minimum polysilicon depletion among oxynitrides. Based on a model in [6], active dopant concentrations at the polysilicon/oxide interface were estimated for these devices and it is concluded that the concentrations are about 5X higher in NH3 and NH3/N2 oxides as compared to control oxide. The reduction in the active dopant concentration at the polysilicon/oxide interface is possibly due to the diffusion of boron across the gate oxide during the drive-in anneal [5]. Accordingly, the suppressed polysilicon depletion in NH3 and NH3/N2 oxides is attributed to nitrogen rich layer at the poly/SiO2 interface, which suppresses the amount of boron from the p<sup>+</sup>-doped polysilicon crossing the interface into the gate oxide.

Fig. 2 shows the quasi-static C-V curves for capacitors with different gate dielectrics. The C-V curve for control oxide is much distorted and shifted to higher  $V_g$  as compared to oxynitrides. The dramatic distortion of C-V curves in control oxides has been attributed to penetration of boron into the substrate and the formation of boron related defect centers [7]. Such distortion is not observed in the oxynitrides, indicating that the boron penetration is suppressed. Among oxynitrides, NH3, NH3/N2 and NH3/O2 oxides show higher interface state density (D<sub>it</sub>) than N<sub>2</sub>O-oxides, as evidenced by the higher values of minimum Cqs. It has been reported that D<sub>it</sub> is actually reduced due to the presence of fluorine caused by  $BF_2$  implantation [8]. Consequently, high values of  $D_{it}$  in NH<sub>3</sub>, NH<sub>3</sub>/N<sub>2</sub> and NH<sub>3</sub>/O<sub>2</sub> oxides are attributed to the NH<sub>3</sub>-nitridation step [9], rather than the effects of boron penetration.

Fig. 3 depicts flatband voltages (V<sub>fb</sub>) of MOS capacitors with various gate dielectrics, for different post-implant anneal temperatures. It is observed that Vfb becomes more positive with increasing anneal temperature, except in the NH<sub>3</sub> and NH<sub>3</sub>/N<sub>2</sub> samples. The V<sub>fb</sub> shifts in positive direction are smaller in all oxynitride gate dielectrics than control oxide. Among oxynitrides, N<sub>2</sub>O oxides show the largest V<sub>fb</sub> shifts. NH<sub>3</sub>, NH<sub>3</sub>/O<sub>2</sub> and NH<sub>3</sub>/N<sub>2</sub> oxides show significantly smaller V<sub>fb</sub> shifts than control and N<sub>2</sub>O oxides. Positive V<sub>fb</sub> shifts in these capacitors can be attributed to a fully depleted layer of penetrated boron, located near the Si/SiO<sub>2</sub> interface [8]. The larger the amount of boron penetration, the larger are the positive  $V_{fb}$  shifts. Consequently, it can be concluded that all oxynitrides under investigation show suppressed boron penetration as compared to control oxides. Moreover, the ability to suppress boron penetration is much improved in NH<sub>3</sub>,  $NH_3/O_2$  and  $NH_3/N_2$  oxides, as compared to  $N_2O$ oxides.

Reduced boron penetration in the substrate in NH<sub>3</sub>,  $NH_3/N_2$  and  $NH_3/O_2$  samples can be attributed to the fact that the amount of boron crossing the poly-gate/SiO<sub>2</sub> interface, itself, is smaller in these samples. Strong nitrogen peaks at the Si/SiO<sub>2</sub> interface in these samples [9] further reduce boron penetration into the substrate, as suggested by Figs. 1 and 2. Nitrogen concentrations both at the Si/SiO<sub>2</sub> and the poly-gate/SiO<sub>2</sub> interfaces in  $N_2O$  oxides are, however, lower [2] as compared to NH<sub>3</sub>, NH<sub>3</sub>/N<sub>2</sub> and NH<sub>3</sub>/O<sub>2</sub> [9]. These effects explain the larger V<sub>fb</sub> shifts in N<sub>2</sub>O oxides than the two NH<sub>3</sub>based oxynitrides. Nevertheless, a finite amount of nitrogen at the Si/SiO2 interface results in a better suppression of boron penetration in N<sub>2</sub>O oxides than the control thermal oxides. It is important to note that high nitrogen concentration near the poly-gate/SiO2 interface, as seen in NH3 and NH3/N2 samples, is crucial in suppressing polysilicon depletion effect as well as Vfb shifts due to boron penetration.

Although NH<sub>3</sub> and NH<sub>3</sub>/N<sub>2</sub> show excellent ability to stop boron penetration, these dielectrics suffer from higher electron trapping [9,10]. On the other hand, although N<sub>2</sub>O oxides and reoxidized NH<sub>3</sub>-nitrided oxides show good hot carrier reliability [3,9,10], they are more susceptible to boron penetration, especially the polysilicon depletion effect. A new technique, namely NH<sub>3</sub>-nitridation of N<sub>2</sub>O-oxides (see Table II), is developed to achieve a highly reliable dielectric with excellent boron stopping potential.

To study the barrier properties of this new gate dielectric,  $V_{fb}$  values after a 30 min 900°C drive-in in N<sub>2</sub> ambient were compared with the corresponding  $V_{fb}$ values of control, N<sub>2</sub>O and O<sub>2</sub>/NH<sub>3</sub> oxides as shown in Fig. 4. It is evident that the boron stopping potential of N<sub>2</sub>O/NH<sub>3</sub> oxides is significantly better than control and N<sub>2</sub>O oxides and is comparable to that of O<sub>2</sub>/NH<sub>3</sub> oxides. The oxide negative charge due to boron penetration was estimated from these V<sub>fb</sub> values after correcting for oxide fixed charge, N<sub>f</sub> [4]. These values are 9.8x10<sup>12</sup>, 2.3x10<sup>12</sup>, 5.6x10<sup>12</sup> and 3.0x10<sup>12</sup> cm<sup>-2</sup> for control, O2/NH<sub>3</sub>, N<sub>2</sub>O and N<sub>2</sub>O/NH<sub>3</sub> oxides, respectively. Thus, the amount of boron penetration in N<sub>2</sub>O/NH<sub>3</sub> is only 30% of that in control and 50% of that in N<sub>2</sub>O oxide. The improvement is attributed to the significant increase in the interfacial [N] due to NH<sub>3</sub>-nitridation, as observed by SIMS.

Charge trapping properties of N<sub>2</sub>O/NH<sub>3</sub> oxides were studied by monitoring the changes in gate voltage  $(\Delta V_g)$  under a constant current density (-100 mA/cm<sup>2</sup>) in MOS capacitors. As shown in Fig. 5, O<sub>2</sub>/NH<sub>3</sub> oxides show a positive  $\Delta V_g$ , indicating significant electron trapping by nitridation induced traps [9]. Nevertheless, even for 20 min NH3-nitridation, N2O/NH3 oxides show only a small increase in electron trapping.  $\Delta V_g$  in O<sub>2</sub>/NH<sub>3</sub> oxides does not show a saturating trend, indicating a significant amount of high-field induced trap generation. On the contrary, despite a severe NH<sub>3</sub>nitridation, trap generation rate in N2O/NH3 oxides is negligible, resulting in superior charge trapping properties. Thus, it is possible to fabricate p-MOSFETs using these gate dielectrics, which show superior hotcarrier reliability, unlike p-MOSFETs with reoxidized NH<sub>3</sub>-nitrided oxides which show worse reliability than those with conventional gate oxides [11]. These observations imply that the trade-off between sufficient [N] for better barrier properties vs. worse electron trapping can be greatly alleviated by this new technique of forming oxynitride gate dielectrics.

Fig. 6 shows Weibull plots for time-to-breakdown ( $t_{bd}$ ) in n<sup>+</sup>-polysilicon gated capacitors with different gate dielectrics. A large degradation in  $t_{bd}$  is observed in  $O_2/NH_3$  oxides after 5 min NH<sub>3</sub>-nitridation. The degradation in  $t_{bd}$  is usually attributed to large electron trapping in these oxides, apparent from Fig. 5. Contrary to such significant degradation in  $t_{bd}$  by NH<sub>3</sub>-nitridation of pure oxides, 20 min NH<sub>3</sub>-nitridation actually increased  $t_{bd}$  in N<sub>2</sub>O-oxides to some extent. NH<sub>3</sub>-nitridation for 5 min degraded charge-to-breakdown Q<sub>bd</sub> (50% failure @ 100 mA/cm<sup>2</sup>) in pure oxides from 50 C/cm<sup>2</sup> to 10.4 C/cm<sup>2</sup>, while 20 min NH<sub>3</sub>-nitridation improved Q<sub>bd</sub> from 89 C/cm<sup>2</sup> to 118 C/cm<sup>2</sup> in N<sub>2</sub>O-oxides.

Interface state generation  $(\Delta D_{it})$  due to constant current stress is plotted in Fig. 7. NH<sub>3</sub>-nitridation increases  $\Delta D_{it}$  in pure oxides. However,  $\Delta D_{it}$  in N<sub>2</sub>O/NH<sub>3</sub> oxides is comparable to the N<sub>2</sub>O oxides. Large  $\Delta D_{it}$  in O<sub>2</sub>/NH<sub>3</sub> oxides is attributed to a distorted interfacial region due to the formation of mismatched Si-N bonds in the Si-O network. However, as seen from Fig. 7, nitrogen incorporation in N<sub>2</sub>O oxides by NH<sub>3</sub>nitridation does not lead to such undesirable effect. This observation suggests that nitrogen incorporation at the interface by NH<sub>3</sub>-nitridation of N<sub>2</sub>O-oxides is somewhat different from that in pure oxides, and is currently under investigation.

## 4. CONCLUSION

In conclusion, a comparative study of boron stopping potential of various oxynitrides is presented based on both polysilicon depletion and  $V_{fb}$ -shift. It is concluded that NH<sub>3</sub> and NH<sub>3</sub>/N<sub>2</sub> oxides show the highest resistance to boron penetration, although these dielectrics show worse hot-carrier reliability properties. To overcome this trade-off between barrier properties vs. hot-carrier reliability, a novel technique, namely NH<sub>3</sub>- nitridation of  $N_2O$  grown oxides, was suggested. It is demonstrated that this technique combines excellent hot carrier reliability of  $N_2O$  oxides and excellent boron stopping potential of NH<sub>3</sub>-nitrided pure SiO<sub>2</sub> and is likely to play an important role in aggressively scaled dual gate CMOS technology.

# 5. REFERENCES

1. G. Q. Lo and D. L. Kwong, IEEE Electron Dev. Lett., <u>EDL-12</u>, 175 (1991)

- 2. H. Hwang et al., IEDM Tech. Dig., 421 (1990)
- 3. H. S. Momose et al., IEDM Tech. Dig., 359 (1991)
- 4. H. Fang et al., IEEE Electron Dev. Lett., <u>EDL-13</u>, 217 (1992)

5. J. S. Cable et al., IEEE Electron Dev. Lett., <u>EDL-</u> <u>12</u>, 128 (1991)

6. C. Y. Wong et al., IEDM Tech. Dig., 238 (1988)

G. Q. Lo et al., Appl. Phys. Lett., <u>57</u>, 2573 (1990)
J. P. Pfiester et al., IEEE Trans. Electron Dev., <u>ED-</u>

37, 1842 (1990)

9. T. Hori et al., IEEE Trans. Electron Dev., <u>ED-34</u>, 2238 (1987)

10. A. B. Joshi et al., IEEE Trans. Electron Dev., <u>ED-</u> 39, 883 (1992)

11. G. J. Dunn and J. T. Krick, IEEE Trans. Electron. Dev., <u>ED-38</u>, 901 (1991)

#### Table I: Gate Dielectric (140 Å) Processing Details

No.	Sample Name	Oxidation	NH3- Nitridation	Post- Nitridation Anneal
1	Control	950°C, O2 Ambient	•	
2	N <sub>2</sub> O	950°C, N <sub>2</sub> O Ambient	•	•
3	NH3	950°C, O2 Ambient	950°C, 60 min	-
3	NH <sub>3</sub> /N <sub>2</sub>	950°C, O2 Ambient	950°C, 60 min	950°C, 30 min, N <sub>2</sub> Ambient
4	NH3/O2	950°C, Oz Ambient	950°C, 60 min	950°C, 30 min, O <sub>2</sub> Ambient



Fig. 1 Polysilicon depletion effect, as monitored by normalized inversion capacitance ( $C_{QS,inv}/C_{ox}$ ) in various gate dielectrics.

3.5

2.5

3

2

1.5

0.5

0

Control

1



Fig. 2 Normalized quasi-static C-V curves for MOS capacitors with control and various oxynitride gate dielectrics.



Fig. 5 Changes in gate voltage required to maintain a constant current density of  $-100 \text{ mA/cm}^2$  in MOS capacitors (area:  $5 \times 10^{-4} \text{ cm}^2$ ) with different gate dielectrics.



Fig. 3 Flatband voltage for MOS capacitors with different gate dielectrics as a function of post-implant drive-in temperatures.

Fig. 4 Flatband voltage in BF<sub>2</sub>-implanted p<sup>+</sup>-polysilicon gate MOS capacitors with different gate dielectrics.

NH<sub>2</sub>

BF<sub>2</sub> Implant:

5.5e15 cm-2, 50 KeV

N<sub>2</sub> Drive-in:

900°C, 30 min

N<sub>2</sub>O

N2O/NH



Fig. 6 Weibull plots of time-to-breakdown in MOS capacitors (area:  $5x10^{-5}$  cm<sup>2</sup>) with different gate dielectrics at a current density of 100 mA/cm<sup>2</sup>.



Fig. 7 Increase in midgap interface state density  $(\Delta D_{it-m})$  in MOS capacitors (area:  $5 \times 10^{-4} \text{ cm}^2$ ) with different gate dielectrics, caused by F-N injection at 2 mA/cm<sup>2</sup> with positive gate bias.