Superior Performance and Reliability of MOSFETs with Ultrathin Gate Oxides Prepared by Conventional Furnace Oxidation of Si in Pure N$_2$O Ambient

W. Ting, G. Q. Lo, J. Ahn, and D. L. Kwong

Microelectronics Research Center
Department of Electrical and Computer Engineering
The University of Texas at Austin, Austin, TX 78712

Abstract - A novel technique for the fabrication of ultrathin MOS gate dielectrics for ULSI applications has been developed by oxidizing Si substrates in pure N$_2$O. This technique has several advantages over conventional thermal oxidation of Si in O$_2$. Si oxidation rate in N$_2$O is significantly lower than in O$_2$, allowing for excellent control of oxide thickness in deep nanometer region. Auger electron spectroscopy (AES) shows that 3 at. % nitrogen piles up at the Si/SiO$_2$ interface, similar to reoxidized nitrided oxides, resulting in a considerable improvement in the immunity to charge trapping and interface state generation and superior time-dependent dielectric breakdown (TDDB) characteristics. MOSFETs with gate oxides grown in N$_2$O exhibit less transconductance degradation under hot electron stressing and superior current drive capability as compared with devices with conventional SiO$_2$ gate dielectrics.

I. Introduction

The requirements on gate oxide quality for MOS devices are becoming more stringent as devices are scaled down into the submicron regime. Recently, we reported the excellent properties of gate oxides prepared by rapid thermal oxidation of Si in N$_2$O.

These oxides exhibit low oxidation rates, superior impurity barrier properties, excellent hot-carrier and x-ray radiation immunity, and improved dielectric wear-out characteristics, as compared with oxides grown in O$_2$.[1-3] The improvements are attributed to nitrogen pile-up at the Si/SiO$_2$ interface.

In the present work, we present a comprehensive study of N$_2$O oxides prepared in a conventional furnace. The results show that this process provides excellent oxide thickness uniformity. In addition, N$_2$O oxides exhibit less charge trapping and interface state generation under constant current stressing, and superior TDDB characteristics as compared with the control oxide.

Finally, n-MOSFETs with N$_2$O gate oxides show higher transconductance for both high and low V$_G$-V$_T$'s and superior endurance under hot-electron stress as compared with MOSFETs having gate oxides grown in O$_2$.

II. Experimental

The starting materials are 4" lightly B-doped Si substrates. Wafers received the standard RCA clean and a final dip in HF solutions prior to oxidation. Oxidation is performed in either pure N$_2$O or pure O$_2$ at 950 °C or 1000 °C. For chemical analysis, Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are performed. Oxide thicknesses are measured by an optical pyrometer. For uniformity study, 22 wafers were loaded into the chamber with a wafer spacing of 5 mm. The thickness data were extracted from six monitor wafers spread evenly through the load.

For device fabrication, control oxides were grown to 62 (MOSFETs) or 68 Å (MOS capacitors) in pure O$_2$ at 950 °C and was subsequently annealed in N$_2$ at the growth temperature. N$_2$O oxides were grown at either 950 °C (MOS capacitors and MOSFETs) or 1000 °C (MOSFETs) to 62 or 61 Å, respectively, and annealed at the growth temperature in N$_2$. Standard phosphorous-doped poly-Si gate technology was used for the fabrication of both MOS capacitors and MOSFETs. A forming gas annealing at 450 °C concludes the device fabrication.

III. Results and Discussion

A. Oxide Composition and Oxidation Kinetics

AES depth profiling was performed on a 62 Å oxide sample prepared at 950 °C in N$_2$O. A nitrogen pile-up at the Si/SiO$_2$ interface is found with a peak concentration of ~ 3 at. % at the interface. The nitrogen concentration at the SiO$_2$ surface or in the bulk is much lower. The interfacial nitrogen-rich layer has been shown crucial to the superior electrical characteristics of reoxidized nitrided oxides, compared to pure SiO$_2$.[4-8] It is believed the interfacial nitrogen reduces strained Si-O bonds thereby enhances the oxide resistances against charge trapping and interface state generation.[4-8] It will be shown later that the charge trapping and interface state generation rates are indeed both reduced in N$_2$O oxides as compared with pure SiO$_2$.

Fig. 1 depicts the thickness of N$_2$O oxides as a function of oxidation time for two temperatures: 950 °C and 1000 °C. For comparison, the oxide thickness from conventional dry oxidation in pure O$_2$ is obtained from SUPREM III simulation. The main difference between oxidation of Si in O$_2$ and N$_2$O is the remarkably reduced oxide growth rates in the latter. This reduction of growth rates is attributed to reduced oxidant partial pressure and nitrogen pile-up at the oxide/substrate interface. During oxidation in N$_2$O, the interfacial nitrogen-rich layer forms gradually which blocks oxidant diffusion toward the substrate. As a consequence, the oxide growth rate is reduced and the oxide thickness gradually saturates as the oxidation time increases.

As shown in Fig. 1, the reduction of oxidation rate is much more pronounced for N$_2$O oxidation than for conventional dry oxidation as the films grow thicker. The slow oxide growth of Si in N$_2$O greatly facilitates the preparation of ultrathin oxide films.

The N$_2$O oxide thickness uniformity is studied. The standard deviation of oxide thickness is 1.4 % of the mean across the load and 1.2 % across the wafer for N$_2$O oxides, compared to 2.8 % and 1.7 % measured from oxides grown in O$_2$ at the same temperature. This demonstrates that the uniformity of furnace-grown N$_2$O oxides is comparable to oxides grown in O$_2$.

B. Time-zero Breakdown

The time-zero breakdown characteristics of oxides grown in both O$_2$ and N$_2$O were obtained by fast-ramping the gate voltage.
of large-area (10-2 cm²) MOS capacitors. Figs. 2 (a) and (b) show the histograms of non-destructive breakdown events defined as the oxide field at which the gate current density is 0.1 mA/cm². The polarity is chosen to bring the substrate into accumulation. As can be seen, the breakdown field distribution of both oxides is similar, indicating the incorporation of nitrogen during oxide growth does not introduce additional defects.

C. Charge Trapping

\[ \Delta V_{th} \] of MOS capacitors under constant current stressing from both polarities are illustrated in Figs. 3 (a) and (b). Compared with control oxides, the electron trapping rates are lower in N₂O oxides as shown by the smaller \( \Delta V_{th} \) 's. The improvement is strongly stress polarity dependent. As shown previously, nitrogen preferentially piles-up at the Si/SiO₂ interface and enhances the structural stability at that interface. Near the gate/SiO₂ interface, however, the nitrogen concentration is low and the compositions of both oxides are similar. Though the gate voltage shift for N₂O oxides is still smaller than that for the control oxide under gate injection, a much more pronounced improvement is seen under substrate injection. The incorporation of nitrogen reduces the strained Si-O bond density which, if broken, forms electron traps.[5] So the formation of Si-H bonds near the Si/SiO₂ interface results in a smaller electron trap density for N₂O oxides there as compared with the control oxide. The nitrogen concentration near the poly-Si/SiO₂ interface is much smaller than at the other interface, so the reduction of electron trapping is less significant.

D. Interface State Generation

The mid-gap interface state density (D̃₆₅) of N₂O and control oxides measured by combined high-low frequency C-V technique on fresh capacitors is 2-4×10¹¹ eV⁻¹ cm⁻². After stressing from either polarity, the D̃₆₅ of N₂O oxides is significantly smaller than that of the control oxide. This is seen in Figs. 4 (a) and (b) where the distortion in quasi-static C-V curves of N₂O oxide is much less than that of the control oxide. The shift of C-V curves is also suppressed for N₂O oxides indicating reduced charge trapping.

E. Time-dependent Dielectric Breakdown

The TDDB characteristics of N₂O oxides are compared with the control oxides both under constant-current and constant-field stressing. QBD's are derived from the former and \( \Delta t_{BD} \)'s are derived from the latter, respectively.

Figs. 5 (a) and (b) illustrate the Weibull probability plots of \( \Delta t_{BD} \) for both oxides under positive- and negative-gate polarity constant-field stresses. Both oxides exhibit comparable \( \Delta t_{BD} \)'s derived from the substrate, however, N₂O oxides demonstrate significantly higher \( \Delta t_{BD} \)'s. The \( \Delta t_{BD} \) distribution is also tighter for N₂O oxides. The time-to-10% breakdowns are reported in Fig. 5 (c). An improvement of approximately one order of magnitude is achieved by oxidation with N₂O. QBD's of both oxides obtained from constant current stressing are shown in Fig. 6. Again, no improvement is seen in N₂O oxides under gate injection, but significant improvement is observed under substrate injection. It is concluded that the TDDB characteristics of N₂O oxides are superior to that of the control oxide under both constant-current and constant-field stressing when electrons are injected from the substrate.

Wu et al. reported similar stress-polarity dependence of TDDB characteristics in reoxidized/nitrided oxides, and this asymmetry was attributed to the distribution of nitrogen.[8] According to Chen et al., TDDB is caused by hole trapping at weak oxide spots. Figs. 2 (a) and (b) illustrate the improved TDDB characteristics under substrate injection. First, the weak oxide spots may be reduced by interfacial nitrogen at the substrate/SiO₂ interface (which is the cathode under substrate injection), although the nature of these weak spots have not been identified. Second, the reduced charge trapping at the substrate/SiO₂ interface relieves the anode field (gate/SiO₂ interface) build-up during constant-current stress under substrate injection. The generation of electron-hole pairs near the anode and the subsequent hole trapping at weak spots near the cathode may be reduced as a consequence.

G. MOSFET Performance and Reliability

The subthreshold slope of MOSFETs is between 70.1 to 70.4 mV/dec for both control and N₂O oxides. These values correspond to average D̃₆₅ between 2-5×10¹⁰ eV⁻¹ cm⁻².

Fig. 7 (a) shows the \( Iₘ-Vₙ \) characteristics of MOSFETs (\( Wₘ/Lₘ=15μm/15μm \)) with gate oxides grown in O₂ and N₂O. The current drive capability of MOSFETs with N₂O gate oxides is enhanced throughout low and high Vₚ regions, comparing with control samples. The enhancement is more pronounced for oxides grown at higher temperature (1000 °C). The normalized transconductance \( gₘ/Cₖ \) in saturation region, which reflects the circuit switching speed[10], is plotted in Fig. 7 (b). A significant improvement of this parameter is achieved in MOSFETs with N₂O gate oxides. A high \( Vₚ-V₁ \) (3.5 V), the \( gₘ/Cₖ \) of N₂O devices is higher than the control device by 15-18 %. In addition, the \( gₘ/Cₖ \) of MOSFETs with N₂O oxides is not saturated up to \( Vₚ-V₁ \) of 3.5 V while control devices exhibit saturated \( gₘ/Cₖ \) in the same bias range. It's worth noting that for MOSFETs with gate oxides nitrided in NH₃, \( gₘ/Cₖ \) is degraded at low \( Vₖ-V₁ \) as compared with devices with pure oxides.[11] This degradation, however, is not seen in N₂O devices.

A similar improvement is observed in the \( gₘ/Cₖ \) of MOSFETs in linear region. As shown in Fig. 8, which plots both \( gₘ \) and \( Iₘ \) normalized by oxide capacitance as a function of \( Vₚ-V₁ \), an improvement is achieved by N₂O oxides for both high and low \( Vₚ-V₁ \)'s. This is contrary to oxides nitrided in NH₃ with or without reoxidization.[11-15] For MOSFETs with nitrided gate oxides, the current drive capability and consequently \( gₘ \) in low \( Vₚ-V₁ \) is degraded. For medium and high \( Vₚ-V₁ \)'s, however, the opposite is observed.

The superior current drive capability of MOSFETs with N₂O gate oxides is attributed to the improved electron mobility. Fig. 9 plots the \( μ_{eff} \) normalized by the maximum \( μ_{eff} \) in MOSFETs with control gate oxides as a function of \( Vₚ-V₁ \). Here \( μ_{eff} \) is defined as \( μ_{eff}=(Vₚ-W_{eff}-C(Vₚ-V₀))/Vₚ \), where \( V₀=0.05 \) V and \( V₁ \) was linear extrapolated. For MOSFETs with N₂O oxide gates, \( μ_{eff} \) is improved by 4-5 % at low \( Vₚ-V₁ \) and -7 % at high \( Vₚ-V₁ \). As a comparison, in MOSFETs with NH₃-nitrided gate oxides, the low-field electron mobility is degraded while the high-field mobility is improved as compared with devices with pure gate oxides.[11-14]

The dependence of \( μ_{eff} \) on gate drive in N₂O system is more pure oxide-like than that of the NH₃-nitrided oxide system because of the lack of peak \( μ_{eff} \) degradation under low gate drive and decreasing the peak mobility under low gate drive.[11] The low nitrogen concentration therefore exercises less impacts on the interface states and results in less significant effects on electron mobility, which explains the smaller improvement of electron mobility under high gate drive.

The lack of peak mobility degradation indicates the proposed increase of interface states located below \( Eₘ \) in nitrided oxide systems may not hold for N₂O oxides systems, and these interface states may even be reduced by the interfacial nitrogen. It indicates that hydrogen instead of nitrogen may be responsible for these
interface states since hydrogen is not involved in the N$_2$O oxidation chemistry. The other possible explanation is the low fixed oxide charge densities (Q$_o$) for N$_2$O oxides. Coulomb scattering by fixed oxide charge is important for lightly inverted surfaces.[17] The Q$_o$ of N$_2$O oxides is approximately 4x10$^{10}$ cm$^{-2}$ compared to 10$^{10}$ cm$^{-2}$ in the control oxides as determined by high-frequency C-V measurements on MOS capacitors. Although Hori found that the peak electron mobility is independent of fixed charge density, the fixed charge densities of his nitrided oxides are higher (in the order of 10$^{11}$ cm$^{-2}$) compared with either the control oxide or the N$_2$O oxide.[11] Nitrogen induced mechanical stress has also been found to modulate electron mobility. Should this model be true for N$_2$O oxides, the improvement of electron mobility throughout the entire gate drive would suggest an increase of tensile stress in the substrate.[18] However, with x-ray diffraction technique we found that for N$_2$O oxides the tensile stress in Si substrate near the Si/SiO$_2$ interface is actually smaller than that for pure SiO$_2$/Si systems.

The reliability of MOSFETs is significantly improved with N$_2$O gate oxides. The transconductance ($g_m$) degradation stressed under maximum substrate current is illustrated in Fig. 10. The stressing with maximum substrate current is chosen to maximize device degradation rates.[19] Again, N$_2$O oxides exhibit significantly improved resistance to $g_m$ degradation over control oxides, especially under lower $V_d$. This dramatic improvement of n-MOSFET endurance is also due to the strengthening of interfacial oxide structures by the interfacial nitrogen which effectively suppresses interface state generation during hot electron stressing.

IV. Conclusion

Properties of SiO$_2$ prepared by furnace oxidation of Si in N$_2$O have been studied. The oxide growth rates in N$_2$O are found to be slower than in O$_2$. AES depth profiling revealed nitrogen pile-up at the Si/SiO$_2$ interface and lower nitrogen concentration elsewhere in the oxide, similar to reoxidized nitrided oxides. XPS confirmed that the interfacial nitrogen bonding state in N$_2$O oxides is similar to the bonding states in N$_2$O oxides prepared by RTP and in LPCVD SiN$_x$. The interfacial nitrogen is believed to reduce dangling Si and strained Si-O bond densities. The oxide interfacial stability is significantly improved as a consequence.

Characterization of MOS capacitors showed that the interface state generation under F-N tunneling stress is suppressed in N$_2$O oxides as compared with the control oxide. Charge trapping and TDDB characteristics are significantly improved under positive gate bias. N-channel MOSFETs with gate oxides grown in N$_2$O show higher transconductance throughout the whole bias range in both linear and saturation regions. This transconductance improvement is attributed to higher electron mobility. Low fixed oxide charge densities and lack of hydrogen are believed to be the cause. Transconductance degradation of n-MOSFET stressed under maximum substrate current is smaller for devices with N$_2$O gate oxides, indicating improved reliability.

Acknowledgement

This work was supported by SRC/SEMATECH under contract No. 88MC505 and Texas Advanced Technology Program.

References


1991 VLSITSA 49
Fig. 1 Oxide thicknesses as a function of oxidation time. The data for dry oxidation in O₂ is obtained by SUPREM simulation.

Fig. 2 Non-destructive breakdown histograms (Iₜ = -0.1 mA/cm²) of oxides grown in (a) O₂ and (b) N₂O. The MOS capacitor area is 10⁻² cm².

Fig. 3 Gate voltage shifts of MOS capacitors during a (a) +100 mA/cm² and (b) -100 mA/cm² constant current stressing. The device area is 5x10⁻⁴ cm².

Fig. 4 Quasi-static C-V curves of (a) control and (b) N₂O oxides before and after a 100 s constant current stressing. The stressing current density is +10 mA/cm². The total dose is 1 Gc/cm².

50 1991 VLSI TSA
Fig. 5 (a) Weibull plots of $Q_{BD}$ measured from MOS capacitors with N$_2$O and control oxide under a +11, 11.5, and 12 MV/cm, (b) $Q_{BD}$ under a -12 MV/cm constant-field stress, and (c) time to 10% failure for both N$_2$O and control oxides under various fields. For (a), open marks are for control oxides and solid marks are for N$_2$O oxides. Squares, circles, and triangles are for stress fields at 11, 11.5, and 12 MV/cm, respectively.

Fig. 6 The Weibull plots of $Q_{BD}$ for control and N$_2$O oxides under ±100 mA/cm$^2$ constant current stressing. Open marks are for the control oxide and solid marks are for N$_2$O oxides. Squares represent $Q_{BD}$'s from substrate injection, and circles are for gate injection.

Fig. 7 (a) $I_d$ - $V_d$ characteristics of MOSFETs (W$_{eff}$/L$_{eff}$=15µm/15µm) with control gate oxides, and N$_2$O gate oxides grown at 950 °C and 1000 °C. (b) $g_m$ normalized by $C_i$ as a function of $V_g$ measured at saturation region ($V_d$=3.5 V).

Fig. 8 $g_m$ and $I_d$ normalized by $C_i$ as a function of gate drive $V_g$ measured in linear region ($V_d$=0.05 V).

Fig. 9 Normalized effective electron mobility $\mu_{eff}$ of MOSFETs (W$_{eff}$/L$_{eff}$=15µm/15µm) as a function of $V_g$-$V_T$. The mobility is normalized by $\mu_{eff,max}$ of the control devices.

Fig. 10 MOSFET transconductance degradation after being stressed at maximum substrate current. The gate oxide of N$_2$O devices was grown at 1000 °C. The transconductance degradation of MOSFETs with gate oxides grown in N$_2$O at 950 °C (not shown) is slightly inferior to that of the 1000 °C N$_2$O oxide devices but is still superior to that of the control oxide devices.