The Electrical Properties of Sub-5-nm Oxynitride Dielectrics Prepared in a Nitric Oxide Ambient Using Rapid Thermal Processing

Z.-Q. Yao, H. B. Harrison, S. Dimitrijevic, *Member, IEEE*, and Y. T. Yeow, *Senior Member, IEEE*

Abstract—Ultrathin (<5 nm) dielectric films have been grown on (100) silicon using rapid thermal processing (RTP) in a nitric oxide (NO) ambient. Interface state density, charge trapping properties, and interface state generation during Fowler-Nordheim electron injection have been investigated. The films grown in NO have excellent electrical properties. These properties are explained in terms of a much stronger and large number of Si-N bonds in both the bulk of the dielectric films and at the Si-SiO₂ interface region. The leakage currents are at least three orders of magnitude lower than other reported results for similar thicknesses. The dielectric films grown in NO ambient are viewed as promising technology for ultrathin dielectrics.

I. INTRODUCTION

GOOD dielectric films are needed for tunnel dielectric of EEPROMs and as gate oxides of MOSFETs amongst many other applications. It has been found that the electric field induced leakage current and interface state density increase in conventional thin oxides after electrical stress, the effect is becoming much more serious with decreasing oxide thickness [1]–[3]. To obtain a high-quality oxide, thermal nitridation of thin SiO₂ in ammonia was proposed to replace the conventional thermal SiO₂ for reasons such as improved dielectric integrity and hot-carrier reliability due to the incorporation of nitrogen at the Si-SiO₂ interface [4]–[6]. On the other hand, the nitrided films were reported to show degraded mobility due to the “heavy” nitridation [4], [7], [8] and increased electron trapping due to the incorporation of hydrogen atoms [6]. Recently, N₂O was proposed and used as an alternative for oxidation and nitridation [9]–[12]. The resulting films show good electrical characteristics; however they have insufficient nitrogen (only ~1–2 atom %) at the dielectric-silicon interface to prevent boron penetration [13]–[15]. We have also found that it is not possible to obtain good quality films below 4 nm using this gas.

Our group has, for the first time, used NO as an alternative oxidation ambient to avoid the disadvantages of NH₃ and N₂O [16], [17]. X-ray photoelectron spectroscopy (XPS) results show that the dielectric films grown in NO have higher nitrogen concentration in both the bulk of the film and also at the dielectric-silicon interface. We have also found that the

growth rates in NO are slow compared to that in N₂O and O₂. This is attributed to the stronger and high concentration of Si-N bond in the NO-grown films. In this paper, we present the electrical properties of these NO-grown films. It is shown that the NO-grown films are superior to O₂- and N₂O- grown films in terms of leakage current, interface state density, and electrical stress induced degradation. For our 3.2 nm films the leakage current is at least 3-order of magnitude lower than that reported for the NH₃- nitrided and pure SiO₂ films of the same thickness [18]–[20].

II. EXPERIMENTAL

1.4–5.0 Ωcm *n*-type (100) silicon wafers were cleaned using both a H₂SO₄/H₂O₂ solution and RCA cleaning process. The wafers were then washed in 1% HF for 60 seconds immediately prior to dielectric film growth. The films were grown in an AG610 rapid thermal processing (RTP) unit. The RTP chamber was purged with ultra high purity N₂ prior to the introduction of NO. The dielectric films were grown in 99.0% NO at 1150°C for 1 to 5 minutes. Some wafers were further exposed to O₂ at the same temperature. These are referred to as reoxidized samples. Comparison was made with films of approximately the same thickness grown in O₂ and N₂O at 950°C for 30 seconds and 300 seconds, respectively. Aluminum gate MOS capacitors (area = 0.01 cm²) were fabricated for electrical characterization.

Thicknesses of the dielectric films in this work, including the pure oxides, were measured using ellipsometry with three angles of incidence (60°, 65°, and 70°). This method allows for the extracting both the film thickness and the refractive index [21]. An HP4145B semiconductor parameter analyzer and an HP4284A LCR meter were used to obtain current-voltage (J-V), high frequency voltage-capacitance (C-V) and small-signal conductance (G-V) characteristics of MOS capacitor before and after positive gate bias Fowler-Nordheim constant-current tunneling stress.

III. RESULTS AND DISCUSSIONS

The growth rate in NO is found to be very low, at 1150°C, the thickness appears to saturate at 3.2 nm within the first 2 minutes [16]. Figs. 1(a) and 1(b) show the high-frequency (100 kHz) C-V and J-V measurement results of the dielectric films grown in NO, N₂O, and O₂. The thicknesses of these films are 3.2 nm, 4.0 nm, and 4.8 nm, respectively, with refractive

Manuscript received June 29, 1994; revised September 22, 1994.

Z.-Q. Yao, H. B. Harrison, and S. Dimitrijevic are with the School of Micro-electronic Engineering, Griffith University, Nathan, QLD 4111, Australia.

Y. T. Yeow is with the Department of Electrical and Computer Engineering, The University of Queensland, St. Lucia, QLD 4072, Australia.

IEEE Log Number 9406932.

TABLE I
THE INTERFACE STATE DENSITIES BEFORE AND AFTER CONSTANT CURRENT STRESS
AND THICKNESS OF DIFFERENT DIELECTRIC FILMS GROWN AT DIFFERENT CONDITIONS

sample labels	growth conditions	film thickness (nm)	interface state density (before stress) ($\times 10^{11}/\text{cm}^2\text{eV}$)	interface state density (after stress) ($\times 10^{11}/\text{cm}^2\text{eV}$)
N_1	at 1150°C in NO for 1 min.	3.0	2.07	2.21
N_2	at 1150°C in NO for 2 min.	3.1	2.03	2.37
N_5	at 1150°C in NO for 5 min.	3.2	2.14	2.40
NN	at 1150°C in NO for 5 min & annealed in N ₂ for 1 min	3.2	1.78	1.81
NO_1	at 1150°C in NO for 5 min & reoxidized at 1150°C in O ₂ for 1 min.	3.6	2.45	2.55
NO_2	at 1150°C in NO for 5 min. & reoxidized at 1150°C in O ₂ for 2 min.	3.8	3.25	3.42
N ₂ O	at 950°C in N ₂ O for 5 min.	4.8	4.12	—
O ₂	at 950°C in O ₂ 30 seconds	4.0	6.26	—

indices of 1.65, 1.50, and 1.46. In the case of the oxide film, there is a distortion in its C-V curve, similar to what was reported previously [18]. This film also has a much larger current through the dielectric compared to the other two films. The J-V plot is however similar to those published elsewhere for the film grown in O₂ with similar thickness [18]–[20]. The N₂O film has better J-V characteristics compared to the oxide, but both this and O₂-grown films show a high tunneling current at bias voltage below 1 V. The film grown in NO has very low leakage current compared to the other two films despite the fact that it is the thinnest. It starts to tunnel for a gate voltage >1.3 V. Its current density is at least 3 orders of magnitude lower than reported results for nitrided and pure oxides of almost the same thickness [18]–[20].

Column 4 in Table I shows the as grown mid-gap interface state densities of different dielectric films measured using the conductance technique [22]. It is seen that the interface state density in the NO samples does not change with growth time. While the midgap interface density of $\sim 2 \times 10^{11} \text{ cm}^{-2}\text{eV}^{-1}$ is one order of magnitude higher than the values expected from thicker electric films used in MOS devices, it is two to three times lower than that seen in ultrathin N₂O and O₂ films. We believe it is a result of slower growth rate which can result in a more “orderly” interface with less silicon dangling bonds and weak oxygen bonds which were believed to form interface states. By annealing in N₂ at 1150°C for 60 seconds the interface state density is reduced to $1.78 \times 10^{11} \text{ cm}^{-2}\text{eV}^{-1}$. In general the interface state density reported here is lower than those reported for dielectrics with the same thickness [18], [23]. It is also known that interface state density increases with decreasing in the dielectric film thickness [23]. We also subjected samples which were grown in NO (1150°C for 5 minutes) to oxidation in O₂ at 1150°C (labelled as NO_1 and NO_2 in Table I). The measurement shows that the interface state densities of these reoxidized samples increases with increasing reoxidation time. This is consistent with the growth in film thickness which leads to a larger number of

Fig. 1. (a) The high frequency (100 kHz) C-V characteristics of the dielectric films grown in NO (at 1150°C for 5 min.), N₂O (at 950°C for 5 min.) and O₂ (at 1150°C for 30s). Area of all the capacitors is 0.01 cm²; (b) the I-V characteristics of the dielectric films as shown in (a).

silicon dangling bonds or weak oxygen-silicon bonds at the Si-SiO₂ interface region.

The charge-trapping behavior of various dielectrics was investigated using a positive gate bias Fowler-Nordheim constant-current stressing of $+5 \mu\text{A}/\text{cm}^2$. The change in gate

Fig. 2. Gate voltage shift of the dielectric films labeled N_5, NN, and NO_2 (details are in Table I) under a constant-current stressing of $+5\mu A/cm^2$ for 300s.

voltage was monitored during stress, and C-V and G-V (conductance-voltage) measurement were performed before and immediately after stressing to determine the change in flat-band voltage and the generation of the interface states (ΔD_{it}) resulting from the stress. During the stress, the changes of gate voltage (ΔV_g) are needed to maintain the constant current. The buildup of positive charge during constant-current stress results in a reduction in V_g to maintain a constant current. Fig. 2 shows the gate voltage shift, ΔV_g , as a function of stress time for an NO grown (N_5) an NO-grown, N_2 annealed (NN), and an NO-grown, reoxidized (NO_2) films. (Samples grown in O_2 and N_2O ambient were found to breakdown almost immediately on applying the constant-current stress). The gate voltages of all these three samples shifted in the negative V_g direction indicating positive charge buildup. The results show that all the ΔV_g saturate in about 200 seconds. The highest ΔV_g of about -0.1 V is observed for reoxidized sample and the lowest of -0.07 V for the nitrogen annealed sample. This agrees with what was stated regarding growth rate and interface states.

It is seen from the results that all the samples grown in an NO environment generally have better electrical characteristics than those grown in either O_2 or N_2O environments. We believe this is due to the higher amount of nitrogen and much stronger Si-N bond in the dielectric films, as we reported previously [16]. Furthermore, we believe that the low growth rate in NO at $1150^\circ C$ will not only reduce the silicon dangling bonds and weak oxygen bonds in the bulk of the film and at the interface, it will also lead to uniform thickness of the film which we believe is the cause of the superior J-V characteristics of our large area (0.01 cm^2) MOS capacitors.

IV. CONCLUSION

We have studied ultrathin dielectric films grown by RTP in an NO ambient. It is found that compared to N_2O and O_2 grown films, the NO-grown films have lower interface state density, reduced tunneling current, and improved resistance to constant current stress. The 3.2-nm film we have investigated would be useful as the tunnel dielectric films in EEPROM. We believe that improvement in dielectric properties through

the use of RTP in an NO ambient could be incorporated into thicker films grown either in NO or in a different ambient and thus make this process attractive for ultrathin MOSFET dielectric applications in ULSI.

REFERENCES

- [1] K. Naruke, S. Taguchi, and M. Wada, "Stress induced leakage current limiting to scale down EEPROM tunnel oxide thickness," in *IEDM Tech. Dig.*, p. 424, 1988.
- [2] P. Olivo, T. N. Ngyyen, and B. Ricco, "High-field-induced degradation in ultrathin SiO_2 films," *IEEE Trans. Electron Devices*, vol. 35, p. 2259, 1988.
- [3] R. Moazzami and C. Hu, "Stress-induced current in thin silicon dioxide films," in *IEDM Tech. Dig.*, p. 92, 1992.
- [4] T. Ito, T. Nakamura, and H. Ishikawa, "Advantages of thermal nitride and nitroxide gate films in VLSI process," *IEEE Trans. Electron Devices*, vol. ED-29, p. 498, 1982.
- [5] T. Hori, H. Iwasaki, Y. Naito, and H. Esaki, "Electrical and physical characteristics of thin nitride oxides prepared by rapid thermal processing," *IEEE Trans. Electron Devices*, vol. ED-34, p. 2238, 1987.
- [6] T. Hori, H. Iwasaki and K. Tsuji, "Electrical and physical characteristics of ultrathin reoxidized nitride oxides prepared by rapid thermal processing," *IEEE Trans. Electron Devices*, vol. ED-36, p. 340, 1989.
- [7] P. Pan, "Characteristics of thermal SiO_2 films during nitridation," *J. Appl. Phys.*, vol. 61, p. 284, 1986.
- [8] K. S. Krisch, B. J. Gross, and C. G. Sodini, "Positive-charge trapping in nitrided oxide and reoxidized nitride gate dielectrics," *J. Appl. Phys.*, vol. 70, p. 2185, 1991.
- [9] H. Fukuda, M. Yasuda, T. Iwabuchi, and S. Ohno, "Novel N_2O -oxynitridation technology for forming high reliable EEPROM tunnel oxide film," *IEEE Electron Device Lett.*, vol. 12, p. 587, 1991.
- [10] J. Ahn, W. Ting, and D.-L. Kwong, "Furnace nitridation of thermal SiO_2 in pure N_2O ambient for ULSI MOS applications," *IEEE Electron Device Lett.*, vol. 13, p. 117, 1992.
- [11] W. Ting, G. Q. Lo, J. Ahn, T. Chu, and D.-L. Kwong, "Comparison of dielectric wear-out between grown in O_2 and N_2O ," in *IEEE Proc. Reliability Phys. Symp.*, p. 323, 1991.
- [12] A. Uchiyama, H. Fukuda, T. Hayashi, T. Iwabuchi, and S. Ohno, "High performance dual-gate sub-halfmicron CMOSFETs with 6-nm-thick nitrided SiO_2 films in an N_2O ambient," in *IEDM Tech. Dig.*, p. 223, 1990.
- [13] A. B. Joshi, J. Ahn, and D.L. Kwong, "Oxynitride gate dielectric for P^+ -polysilicon gate MOS devices," *IEEE Electron Device Lett.*, vol. 14, p. 560, 1993.
- [14] T. Hori, "Nitrided gate-oxide CMOS technology for improved hot-carrier reliability," in *Microelectronic Engineering*, vol. 22, p. 245, 1993.
- [15] G. W. Yoon, A. B. Joshi, J. Kim, and D. L. Kwong, "MOS characteristics of NH_3 nitrided N_2O -grown oxides," *IEEE Electron Device Lett.*, vol. 14, p. 179, 1993.
- [16] Z.-Q. Yao, H. B. Harrison, S. Dimitrijevic, Y. T. Yeow, and D. Sweatman, "High quality ultra thin dielectric films grown on silicon in a nitric oxide ambient," *Appl. Phys. Lett.*, vol. 64, p. 3548, 1994.
- [17] H. B. Harrison, A. Misiura, S. Dimitrijevic, D. Sweatman, Z.-Q. Yao, and Y. T. Yeow, "Dielectrics on silicon thermally grown or annealed in a nitrogen rich environment," presented at the spring meeting of MRS in San Francisco, April 1994, published in *Digest of Technical Papers*.
- [18] M. Depas, R. L. Van Meirhaeghe, W. H. Lafere, and F. Cardon, "Electrical characteristics of $Al/SiO_2/n$ -Si tunnel diodes with an oxide layer growth by rapid thermal oxidation," *Solid-State Electronics*, vol. 37, p. 433, 1994.
- [19] S. Naggano, M. Tsukiji, K. Ando, E. Hasegawa, and A. Ishitani, "Mechanism of leakage current through the nanoscale SiO_2 layer," *J. Appl. Phys.*, vol. 75, p. 3530, 1994.
- [20] T. Nguyen, D. A. Carl, S. V. Nguyen, D. M. Dobuzinsky, and J. W. Korejwa, "New leakage mechanism in sub-5 nm oxynitride dielectrics," *Appl. Phys. Lett.*, vol. 63, p. 1972, 1993.
- [21] T. S. Chao, W. H. Chen, S. C. Sun, and H. Y. Chang, "Characterizations of oxide grown by N_2O ," *J. Electrochem. Soc.*, vol. 140, p. 2905, 1993.
- [22] E. H. Nicollian and J. R. Brews, *MOS Physical and Technology*. New York: Wiley, 1982.
- [23] H. Fukuda, M. Yasuda, T. Iwabuchi, S. Kaneko, T. Ueno, and I. Ohdomari, "Process dependence of the $SiO_2/Si(100)$ interface trap density of ultra thin SiO_2 films," *J. Appl. Phys.*, vol. 72, p. 1906, 1992.