Improvement in electrical characteristics of high- k Al_2O_3 gate dielectric by field-assisted nitric oxidation

Kai-Chieh Chuang and Jenn-Gwo Hwu^{a)}

EE-II, R446, Department of Electrical Engineering and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei 10617, Taiwan, Republic of China

(Received 10 May 2006; accepted 19 October 2006; published online 6 December 2006)

The authors perform a simple technique for the improvements in both current density reliability of high- k Al_2O_3 gate dielectrics. An Al_2O_3 was prepared by chemical oxidation at an appropriate electrical field in nitric acid at room temperature then furnace annealed at 650 °C in N_2 . The interface trap-induced capacitance was used to investigate the interfacial property between the gate dielectric Si substrate. On the other hand the stress induced leakage current (SILC) was measured for characterizing the property of bulk oxide. It was found that the electrical characteristics of bulk oxide including leakage breakdown field SILC, were much improved without sacrificing interfacial property. The improvement can be ascribed to the compensation oxidation process. © 2006 American Institute of Physics. [DOI: 10.1063/1.2402215]

High- k dielectrics are being considered as a possible replacement for SiO_2 as conventional oxide thickness scaled into a regime where direct tunneling current dominates the gate leakage.^{1–4} However, some issues associated with high- k gate dielectrics, such as flatband voltage shift and stress-induced leakage current (SILC), are still hurdles for reliable high- k gate dielectrics.⁵ Several methods were proposed to improve high- k gate dielectrics such as N_2 plasma treatment,⁶ fluorine incorporation,⁷ and multiple gate stacks.⁸ Here, we introduce a simple technique to improve high- k Al_2O_3 gate dielectrics. Al_2O_3 is a widely investigated gate dielectric with benefits in many aspects⁹ and can be formed in nitric acid at room temperature without oxidizing silicon.¹⁰ In this work, metal-oxide semiconductor (MOS) capacitors with Al_2O_3 prepared on Si substrate by field-assisted HNO_3 oxidation (FA- HNO_3) were investigated. MOS capacitors with Al_2O_3 prepared by only nitric oxidation and SiO_2 prepared by rapid thermal oxidation (RTO) were also fabricated for comparison. The results show that samples prepared by field-assisted oxidation with HNO_3 exhibit excellent electrical properties and reliability characteristics. It is believed that electrical field enhances oxidation process, and thus reduces weak spots and imperfect bondings.¹¹

p -type (100)-oriented Si wafers were treated by modified RCA clean. Ultrathin SiO_2 was grown by RTO. The thickness of RTO SiO_2 was about 8–10 Å as measured by an ellipsometer. 99.9999% pure Al was thermally evaporated onto the silicon surface with thicknesses of 13–16 Å. These samples were divided into group I (FA- HNO_3) and group II (HNO_3). Group I was immersed in diluted HNO_3 ($\text{HNO}_3:\text{H}_2\text{O}=1:19$) with an applied electrical field of 5 V/cm for 60 s. Platinum plates were used as the electrodes. Postoxidation annealing was implemented in the furnace at 650 °C in N_2 for 60 s. After Al deposition, the $2.25 \times 10^{-4} \text{ cm}^2$ Al gate was defined by conventional photolithography and wet etching. The underside of each wafer was coated with an aluminum film to form MOS capacitors

after native oxides were removed. Group II was fabricated in the same condition but without applying electrical field during nitric oxidation step.

I - V and C - V measurements were performed by an HP4140B picoampere meter and an HP 4284 precision impedance meter, respectively. Equivalent oxide thickness (EOT) was extracted by fitting the 1 kHz C - V curve under the consideration of a quantum mechanical effect.¹²

Figure 1 displays the 1 MHz and 1 kHz C - V curves of all samples. The trap densities calculated by the 1 MHz C - V curves are 2.02×10^{10} , 2.62×10^{11} , and $1.34 \times 10^{11} \text{ cm}^{-2}$ of FA- HNO_3 , HNO_3 , and RTO samples, respectively. Theoretical simulation curves are also demonstrated to extract EOT. The EOTs of FA- HNO_3 and HNO_3 samples are 2.5 and 2.7 nm, respectively. This means that applying electrical field makes Al_2O_3 thin film more compact without increasing interfacial layer. On the other hand, the 1 kHz C - V curve of HNO_3 sample distorted at large negative bias because of oxide traps at different energy levels. The hump of the 1 kHz curves in the depletion region originates from the interface states that provides interface trap induced capacitance connected with oxide capacitance C_{ox} in series. By examining the C - V curves in the depletion region, it can be seen that all

FIG. 1. C - V curves of (a) field-assisted nitric oxidation $\text{Al}_2\text{O}_3/\text{SiO}_2$ (FA- HNO_3) and (b) nitric oxidation $\text{Al}_2\text{O}_3/\text{SiO}_2$ (HNO_3) and (c) RTO samples at 1 MHz and 1 kHz. Theoretical curves considering quantum mechanical effect are also shown.

^{a)} Author to whom correspondence should be addressed; electronic mail: hwu@cc.ee.ntu.edu.tw

FIG. 2. Weibull plots of interface trap induced capacitance C_{it} at flatband voltage for FA-HNO₃ Al₂O₃/SiO₂, HNO₃ Al₂O₃/SiO₂, and RTO SiO₂ samples.

FIG. 3. Relationship between the gate injection current density at $V_G - V_{FB} = -1$ V and equivalent oxide thickness for FA-HNO₃ Al₂O₃/SiO₂, HNO₃ Al₂O₃/SiO₂, RTO SiO₂, and anodization (ANO) SiO₂ oxides.

FIG. 4. Accumulative plots of oxide breakdown field of FA-HNO₃ Al₂O₃/SiO₂ and HNO₃ Al₂O₃/SiO₂ stacked oxides. Typical J - V curves for two kinds of samples are shown in the inset.

FIG. 5. Gate leakage currents before and after constant current stress of -10 mA/cm² for (a) FA-HNO₃ and (b) HNO₃ samples.

samples had comparable interface state density qualitatively. Furthermore, Fig. 2 shows the Weibull plots of the interface trap induced capacitance at flatband voltage, which is calculated by modified high-low frequency method.⁹ Their interfacial properties are quite similar. This can be attributed to the initial RTO oxide formation.

Figure 3 compares the gate injection current densities at $V_G - V_{FB} = -1$ V as a function of EOT for RTO oxides, anodization (ANO) oxides, FA-HNO₃ Al₂O₃/SiO₂, and HNO₃ Al₂O₃/SiO₂. The leakage currents of both FA-HNO₃ Al₂O₃/SiO₂, and HNO₃ Al₂O₃/SiO₂ are at least one order of magnitude lower than pure SiO₂ oxides. This confirms the basic characteristics of high- k dielectrics. On the other hand, the leakage current of FA-HNO₃ samples and HNO₃ samples are compatible while the FA-HNO₃ samples are 2 Å thinner than HNO₃ samples. This result accounts for the better bulk oxide properties of FA-HNO₃ samples than the other.

Figure 4 shows the time-zero dielectric breakdown (TZDB) endurance of FA-HNO₃ and HNO₃ samples. The J - V is also shown in the inset. It is noted that the equivalent breakdown fields of stacked oxides prepared by FA-HNO₃ with EOT=2.5 nm are better than those prepared by HNO₃. This can be ascribed to the better bulk oxide properties that are consistent with the percolation model which is often used to explain breakdown phenomenon.

Finally, charge trapping characteristic of Al₂O₃ gate dielectric is investigated by constant current stress as shown in Fig. 5. The stressed current density is -10 mA/cm² for 120 s. The SILC is measured immediately after stress being removed. Considerable increase is observed for HNO₃ sample as shown in Fig. 5(b) at about $V_G = -1$ V, which corresponds to the flatband voltage. This increase is probably due to bulk oxide trap generation as caused by the electrical stress.¹³ However, little increase is observed except for the V_{FB} around. This suggests that the stressed induced defects are localized.

The field-assisted nitric oxidation can improve Al₂O₃ bulk property. This can be explained qualitatively. Chemical oxidation is a fast, nonuniform process that often results in oxygen vacancy¹⁴ and imperfect bonds. If we apply an electrical field during the oxidation process, the weak spots will be fixed automatically. That is, when the oxide forms, it becomes less conductive locally, and therefore most of the NO₃⁻ ions will impose elsewhere. Thus the insulator is more compact and perfect while keeping minimized interface states.

In this work, a simple technique of applying electrical field during chemical oxidation process is demonstrated. It is found that the electrical characteristics of bulk oxide were much improved while the interface states were kept minimized. The improvement can be ascribed to the compensation effect during field-assisted oxidation process.

This work was supported by the National Science Council, ROC, under Contract No. NSC94-2215-E-002-004.

¹J. H. Lee, K. Koh, N. I. Lee, M. H. Cho, Y. K. Kim, J. S. Jeon, K. H. Cho, H. S. Shin, M. H. Kim, K. Fugihara, H. K. Kang, and J. T. Moon, Tech. Dig. - Int. Electron Devices Meet. **2000**, 645.

²H. J. Osten, J. P. Liu, P. Gaworzewski, E. Bugiel, and P. Zaumseil, Tech. Dig. - Int. Electron Devices Meet. **2000**, 653.

³A. Nakajima, Q. D. M. Khosru, T. Yoshimoto, T. Kidera, and S. Yokoyama, Appl. Phys. Lett. **80**, 1252 (2002).

⁴L. Kang, B. H. Lee, W. J. Qi, Y. Jeon, R. Nieh, S. Gopalan, K. Onishi, and J. C. Lee, IEEE Electron Device Lett. **21**, 181 (2000).

- ⁵S. I. Lee, S. J. Risee, R. Clark, and D. L. Kwong, Digest of Technical Papers—Symposium on VLSI Technology, **2002**, 78.
- ⁶C. W. Yang, Y. K. Fang, S. F. Chen, C. Y. Lin, M. F. Wang, Y. M. Lin, T. H. Hou, L. G. Yao, S. C. Chen, and M. S. Liang, Electron. Lett. **39**, 421 (2003).
- ⁷K. I. Seo, R. Sreenivasan, P. C. McIntyre, and K. C. Saraswat, Tech. Dig. - Int. Electron Devices Meet. **2005**, 417.
- ⁸F. Zhu, S. J. Rhee, C. Y. Kang, C. H. Choi, M. S. Akbar, S. A. Krishnan, M. Zhang, H. S. Kim, T. Lee, I. Ok, and J. C. Lee, IEEE Electron Device Lett. **26**, 876 (2005).
- ⁹S. W. Huang and J. G. Hwu, IEEE Trans. Electron Devices **50**, 1658 (2003).
- ¹⁰S. Wolf and R. N. Tauber, *Silicon processing for the vlsi era: Process Technology* (Lattice, Sunset Beach, CA, 1986), Vol. 1, p. 534.
- ¹¹Y. H. Shih and J. G. Hwu, IEEE Electron Device Lett. **20**, 545 (1999).
- ¹²K. Yang, Y. C. King, and C. Hu, VLSI Tech. Dig. **1999**, 77.
- ¹³F. Crupi, R. Degraeve, A. Kerber, D. H. Kwak, and G. Groeseneken, IEEE Int. Reliab. Phys. Symp. Proc. **2004**, 181.
- ¹⁴N. J. Seong, S. G. Yoon, S. J. Yeom, H. K. Woo, D. S. Kil, J. S. Roh, and H. C. Sohn, Appl. Phys. Lett. **87**, 132903 (2005).