

## Superior Damage-Immunity of Thin Oxides Thermally Grown on Reactive-Ion-Etched Silicon Surface in $N_2O$ Ambient

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**Abstract**—Thin oxides thermally grown on reactive-ion-etched silicon surfaces in  $N_2O$  ambient have been studied. As compared with pure oxides grown on the etched silicon in dry oxygen,  $N_2O$ -grown oxides exhibit significantly stronger immunity to the RIE-induced damages. A great improvement in both time-zero-dielectric-breakdown (TZDB) and time-dependent-breakdown (TDDB) characteristics is observed for the  $N_2O$ -grown oxides on RIE-treated silicon surfaces. Accelerated tests have shown that the  $N_2O$  oxide grown on the RIE silicon surface can achieve a lifetime longer than the pure oxide grown on the correspondingly etched silicon surface with a factor over  $10^8$ .

### I. INTRODUCTION

As device dimensions get smaller, a high definition etching technique, such as reactive ion etching (RIE), is required. Hence, the effects of RIE processes have been widely studied for the ultra-large-scale-integrated (ULSI) technology. For advanced semiconductor devices, such as tunnel oxides for electrically erasable read-only memory (EEPROM) devices and dielectrics for trench capacitors, thin thermal oxides are frequently grown on a RIE-treated silicon surfaces. Due to the ion bombardment, the induced damages in the silicon can not be avoided during the dry etching. The quality of thin thermal oxides grown on the RIE-treated silicon will be therefore degraded by these residual defects. Many authors [1], [2] have studied on the issues of damages induced by the RIE. On the other hand, the benefits of  $N_2O$ -grown oxides have also been extensively studied in the past few years. Strong interface stability, low electron traps, and large charge-to-breakdown have been observed by many authors [3], [4] for the  $N_2O$  oxides. In this letter, the damage-immunity of the thin oxide grown on the reactive-ion-etched silicon surface in  $N_2O$  ambient will thus be proposed.

### II. EXPERIMENTAL PROCEDURES

(100) oriented, 2.5–3.5  $\Omega$ -cm, boron-doped silicon wafers were used. At first, 350  $\text{\AA}$ -thick oxides were grown in  $O_2$  ambient at 900°C. To introduce the damages on the silicon surface, the oxide stripping was performed by a RIE system. A two-step oxide-etching recipe using  $CHF_3/CF_4/Ar$  and  $CF_4/O_2$  was employed. After the oxide etching, thermal oxides ( $\sim 80 \text{\AA}$ ) were grown at 900°C in  $N_2$ -diluted  $O_2$  and wholly  $N_2O$  ambient, respectively. Some samples without RIE treatments were accompanied for each run to evaluate the impacts of the defects induced by the RIE. Subsequently, an *in situ* post-oxidation annealing was performed in  $N_2$  ambient at 900°C for 10 min. After a 4000  $\text{\AA}$ -thick polysilicon deposition and subsequent  $POCl_3$  diffusion, MOS capacitors were fabricated to analyze the characteristics of the dielectrics.

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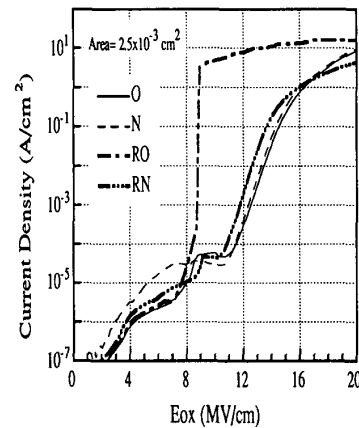


Fig. 1. Curves of current density ( $J$ ) versus electrical field ( $E_{ox}$ ) obtained by the voltage ramping technique with a ramping rate of 1 V/s.

### III. RESULTS AND DISCUSSION

In order to avoid the effects of high-temperature annealing, pure oxides were grown in  $N_2$ -diluted  $O_2$  ambient to keep the oxidation time comparable to that for the  $N_2O$ -oxidation process. The time for dry oxidation and  $N_2O$ -oxidation are 85 min and 78 min, accordingly. The dependence of current density ( $J$ ) on electrical field ( $E_{ox}$ ) for different dielectrics are shown in Fig. 1. It is clearly noted in this figure that the sample RO, with pure oxide grown on the RIE-treated silicon, exhibits a remarkable degradation. Due to the ion bombardment from RIE, contaminations and damages will be induced on the silicon surface [5], [6]. As is well known, surface stacking faults via the contaminations can occur after high-temperature oxidation for RIE samples, which degrade the oxide breakdown voltages [5]. Therefore, the damages induced by RIE is conjectured as the main cause for the early breakdown events of the sample RO. On the contrary, the sample RN, i.e.,  $N_2O$ -oxide grown on the RIE-treated silicon, displays a great improvement over the sample RO in the leakage currents and breakdown fields. It indicates that thermal oxides grown on the RIE-treated silicon surface in  $N_2O$  atmosphere can remedy the RIE-induced defects. The cumulative distributions of TZDB characteristics for various dielectrics are shown in Fig. 2. Oxide breakdown field ( $E_{bd}$ ), is defined as the electrical field at which the gate current reaches to 1 mA/cm<sup>2</sup>. For the samples without RIE, pure oxide, O, and  $N_2O$  oxide, N, show no difference in TZDB characteristics. These results were consistent with what have been reported [3], [4] that  $N_2O$ -grown oxides and pure oxides have similar TZDB characteristics. However, for the RIE-treated specimens, the sample RN possess higher breakdown fields and tighter distribution than the sample RO. Furthermore, the breakdown field and its distribution of the sample RN are similar to those of the sample N and O. Lots of AES and SIMS [7] data have shown that nitrogen pileup near the interface exists for the  $N_2O$ -grown oxides. It is believed that these nitrogen atoms must play an important role to passivate the RIE-induced damages.

Fig. 3 shows the time-to-breakdown ( $t_{BD}$ ) characteristics of the MOS capacitors (area =  $1.6 \times 10^{-3} \text{ cm}^2$ ) for various dielectrics under a constant voltage stressing of 13 MV/cm. The sample O and N also show a narrow-range distribution and little difference in  $t_{BD}$ , as was reported by other authors [3]. It indicates that the oxidation

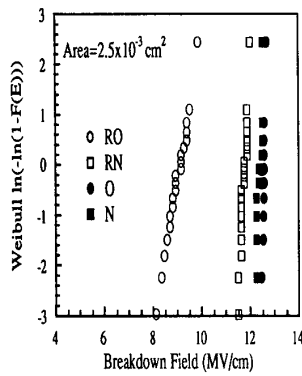


Fig. 2. Cumulative probabilities of the time-zero dielectric-breakdown characteristics using voltage ramping technique for the MOS capacitors with an area of  $2.5 \times 10^{-3} \text{ cm}^2$ . Breakdown field is defined as the field at which the gate current density reaches to  $1 \text{ mA/cm}^2$ .

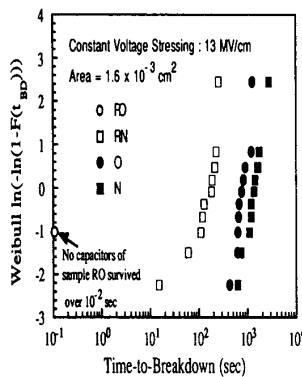


Fig. 3. Weibull plots of the time dependent dielectric breakdown (TDDB) characteristics at a constant stressing electrical field of  $13 \text{ MV/cm}$  for the capacitors with various dielectrics.

environment, including initial cleaning and device fabrication, is normal in this experiment. On the other hand, the RIE-treated samples show a significant difference between pure oxides and  $\text{N}_2\text{O}$ -grown oxides in TDDB characteristics. From the data, no capacitor of the sample RO survives over  $10^{-2} \text{ s}$  with a constant field stressing at  $13 \text{ MV/cm}$ . In contrast, the sample RN exhibits a tolerable range of  $t_{BD}$  and a distribution for practical applications. According to the TDDB model [8], the early breakdown is caused by the weak spots from the high density of hole traps at the cathode, thinner oxide thickness, lower barrier height due to the contamination, or crystalline defects. The improved TDDB characteristics of  $\text{N}_2\text{O}$ -grown oxides are attributed to the nitrogen pileup at interface with reducing dangling bond densities of Si and strained Si-O [3]. Therefore, the weak spots at the  $\text{SiO}_2/\text{Si}$  interface caused by RIE treatment are strengthened.

In order to compare the lifetime of  $\text{N}_2\text{O}$  oxides and pure oxides grown on the RIE-treated Si surface, accelerated TDDB tests [9] were demonstrated. The  $\log(t_{BD})$  versus  $1/E$  plots of the sample RO and RN are shown in Fig. 4. The slopes,  $G$ , of the projection lines for the sample RO and RN are  $360 \text{ MV/cm}$  and  $352 \text{ MV/cm}$ , respectively. They are close to the data reported by Chen *et al.* ( $320 \text{ MV/cm}$ ) [10]. The dielectric lifetimes of the sample RO and RN were then projected by extrapolating the TDDB projection curve at the  $E_{OX} = 8 \text{ MV/cm}$ . The  $t_{BD}$  of the sample RN is estimated to have about nine orders as large as that of the sample RO.

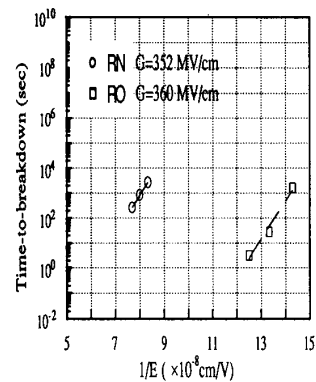


Fig. 4. TDDB data and projection lines of the capacitors for the samples RN and RO.

IV. SUMMARY AND CONCLUSIONS

Thin  $\text{N}_2\text{O}$ -oxides grown in  $\text{N}_2\text{O}$  ambient have been shown to exhibit superior immunity to the RIE-induced damages than pure oxides. This process could provide higher breakdown fields, lower leakage current, and significantly improved TDDB characteristics for the thermal oxides on the RIE-treated silicon substrates. The  $\text{N}_2\text{O}$ -oxides grown on the etched Si surface could achieve a quality comparable to the thermal oxides grown on nonetched wafers. Therefore,  $\text{N}_2\text{O}$ -grown oxides will be a promising candidate for the future ULSI application, especially the subsequent oxidation after the RIE process.

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REFERENCES

- [1] S. W. Pang, D. D. Rathman, D. J. Siliversmith, R. W. Mountain, and P. D. DeGraff, "Damage induced in Si by ion milling or reactive ion etching," *J. Appl. Phys.*, vol. 54, no. 6, pp. 3272, 1983.
- [2] X. C. Mu, S. J. Fonash, G. S. Oehrlein, S. N. Chakravarti, C. Parks, and J. Keller, "A study of  $\text{CClF}_3/\text{H}_2$  reactive ion etching damage and contamination effects in silicon," *J. Appl. Phys.*, vol. 59, no. 8, p. 2958, 1986.
- [3] W. Ting, G. Q. Lo, J. Ahn, and D. L. Kwong, "MOS characteristics of ultrathin  $\text{SiO}_2$  prepared by oxidizing Si in  $\text{N}_2\text{O}$ ," *IEEE Electron Device Lett.*, vol. 12, p. 416, 1991.
- [4] W. Ting, G. Q. Lo, J. Ahn, T. Chu, and D. L. Kwong, "Comparison of dielectric wear-out between oxides grown in  $\text{O}_2$  and  $\text{N}_2\text{O}$ ," *Proc. IEEE Reliability Phys. Symp.*, 1991, p. 323.
- [5] F. K. Moghadam and X.C. Mu, "A study of contamination and damage on Si surfaces induced by dry etching," *IEEE Trans. Electron Devices*, vol. 36, p. 1602, 1989.
- [6] H. P. Strunk, H. Cerva, and E. G. Mohr, "Damage to the silicon lattice by reactive ion etching," *J. Electrochem. Soc.*, vol. 135, p. 2877, 1988.
- [7] G. Weidner and D. Kruger, "Nitrogen incorporation in  $\text{SiO}_2$  by rapid thermal processing of silicon and  $\text{SiO}_2$  in  $\text{N}_2\text{O}$ ," *Appl. Phys. Lett.*, vol. 62, p. 294, 1993.
- [8] I. C. Chen, S. Holland, and C. Hu, "Electrical breakdown in thin gate and tunneling oxide," *IEEE Trans. Electron Devices*, vol. ED-32, p. 413, 1985.
- [9] I. C. Chen and C. Hu, "Accelerated testing of time-dependent breakdown of  $\text{SiO}_2$ ," *IEEE Electron Device Lett.*, vol. 8, p. 140, 1987.