

# High Quality Interpoly Dielectrics Deposited on the Nitrided-Polysilicon for Nonvolatile Memory Devices

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**Abstract**—High quality interpoly dielectrics have been fabricated by using  $\text{NH}_3$  and  $\text{N}_2\text{O}$  nitridation on polysilicon and deposition of tetra-ethyl-ortho-silicate (TEOS) oxide with  $\text{N}_2\text{O}$  annealing. The surface roughness of polysilicon is improved and the value of weak bonds is reduced due to nitrogen incorporation at the interface, which improves the integrity of interpoly dielectrics. The improvements include a higher barrier height, breakdown strength, and charge-to-breakdown, and a lower leakage current and charge trapping rate than counterparts. It is found that this method can simultaneously improve both charge-to-breakdown (up to  $20 \text{ C/cm}^2$ ) and electric breakdown field (up to  $17 \text{ MV/cm}$ ).

**Index Terms**—Barrier height, charge-to-breakdown, dielectric, electric breakdown field, interpoly, nonvolatile memories, polysilicon.

## I. INTRODUCTION

THERMALLY grown or deposited oxides on  $n^+$  polysilicon have been used as the inter-dielectric for nonvolatile memories such as erasable-programmable read-only memory (EPROM), electrical-erasable programmable read-only memory (EEPROM), and flash memories. In order to obtain good data retention and endurance characteristics, inter-dielectrics with a low conductivity (low leakage current) and a high electric breakdown field ( $E_{bd}$ ) have been topics of research for a long time [1]–[3]. Because thermal oxidation of polysilicon leads to a rough polysilicon surface, thermally grown polyoxides exhibit a lower dielectric strength and a higher leakage current than those of oxide grown on single crystal silicon [4]–[12]. Recently, in contrast to thermal oxides, deposited dielectric layers have been investigated as a very promising alternative, since these dielectric layers are deposited on the polysilicon layer without silicon consumption. Consequently, the surface of polysilicon for a deposited polyoxide structure is found to be smoother than oxidizing counterpart. Low-temperature oxides (LTO) with an annealing in a rapid thermal processing (RTP) system or oxides deposited in a low-pressure chemical-vapor-deposition (LPCVD) system

have been used, but resultant electrical properties of LTO are not good enough for EEPROM applications even with additional postdeposition treatments [13]–[15]. In contrast to LTO, dielectrics deposited at a high temperature, like tetra-ethyl-ortho-silicate (TEOS), exhibit an improved performance [16]–[18]. In addition, high-temperature oxides (HTO) with the postdeposition treatment in a rapid thermal annealing (RTA) system are proposed to improve electrical properties, which can achieve effects of densification, reoxidation, and nitridation [19]–[21]. Furthermore, Klootwijk *et al.* [19] found that the oxide deposited with an additional  $\text{N}_2\text{O}$ -annealing is an attractive alternative for conventional polyoxide, which results in an improved endurance of EEPROM devices by a factor of ten.

The underlying polysilicon layer also plays a dominant role in the dielectric strength. Lei *et al.* [22], [23] found that the strength of deposited dielectric depends on the roughness of polysilicon. Using chemical-mechanical polishing (CMP) on polysilicon, the dielectric integrity is significantly improved due to the smooth interface of the polysilicon, but charge-to-breakdown ( $Q_{bd}$ ) values are not improved simultaneously [23]. The method using both CMP and CVD oxide yields a high breakdown field ( $E_{bd}$ ) and low electron-trapping rate. Recent reports show that the reliability of MOS and polyoxide capacitors can be improved by introducing proper amounts of nitrogen or fluorine [1], [24], [25]. It is also reported that the  $\text{N}_2\text{O}$ -grown and  $\text{N}_2\text{O}$ -annealing polyoxides have better electrical performances than  $\text{O}_2$ -grown polyoxides, which contributes to the nitrogen incorporation at the polyoxide/polysilicon interface [21], [26]–[29]. However, this treatment moderately improves the dielectric strength only.

In this paper, polyoxides are fabricated by utilizing a  $\text{NH}_3$ -nitridation and RTA  $\text{N}_2\text{O}$ -annealing on polysilicon to incorporate nitrogen at the surface of polysilicon. TEOS-oxides are then deposited on this nitrided polysilicon and followed with or without a densification in an  $\text{N}_2\text{O}$  ambient. It is found that this method can simultaneously improve both  $Q_{bd}$  and  $E_{bd}$ .

## II. EXPERIMENTS

The  $n^+$ -polysilicon/polyoxide/ $n^+$ -polysilicon capacitors were fabricated on the p-type (100) silicon wafers. First, silicon wafers were thermally oxidized at  $1000^\circ\text{C}$  to form a 100-nm-thick isolation oxide. Then a 300-nm polysilicon layer (poly-1) was deposited in a LPCVD system using  $\text{SiH}_4$  gas at  $620^\circ\text{C}$  and subsequently doped with  $\text{POCl}_3$  at  $900^\circ\text{C}$  for 30 min, resulting in a sheet resistance of  $30\sim 40 \Omega/\square$ . After the p-glass was stripped off, the samples were then annealed

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in NH<sub>3</sub> ambient at 800 °C for 2 h followed with or without a N<sub>2</sub>O-RTA annealing at 800 °C for 20 s. After that, a TEOS oxide with thickness to 100 Å was deposited in a LPCVD system at 650 °C, followed by a RTA at 900 °C for 30 s in the N<sub>2</sub> or N<sub>2</sub>O ambient for densification of oxides to a final 90 Å. Then a second polysilicon layer (poly-2) of 300-nm was deposited by a LPCVD system at 620 °C and doped to a sheet resistance of 30~40 Ω/□ with the same POCl<sub>3</sub> process as poly-1. After definition of the poly-2, all samples were covered with a 100-nm oxide as a passivation layer. Contact holes were opened and aluminum was deposited and patterned to form the final capacitor structures. Finally, all devices were sintered at 400 °C for 30-min in a N<sub>2</sub> ambient.

Atomic force microscope (AFM) was used to characterize the surface morphology of polysilicon films with or without nitridation. Polyoxide thickness was determined by the high-frequency capacitance-voltage measurements with Keithley 590 and 595. The electrical properties, effective electron barrier height, electron trapping characteristics, and charge-to-breakdown were measured by a HP-4145B semiconductor parameter analyzer.

### III. RESULTS AND DISCUSSION

Impacts of nitridation on poly-1 and densification of TEOS in N<sub>2</sub>O are evaluated by the measurement of current–voltage (*I*–*V*) and breakdown field. In this measurement, the poly-2 is positively biased. (i.e., electrons are injected from the dielectric/poly-1 interface). Fig. 1(a) shows curves of current density versus electrical field, and Fig. 1(b) depicts the Weibull distributions of breakdown field for 75 capacitors corresponding to Fig. 1(a). The electrical field (*E*<sub>ox</sub>) is defined as *V*<sub>g</sub>/*T*<sub>ox</sub>, where *V*<sub>g</sub> is the applied gate voltage, and *T*<sub>ox</sub> is the effective dielectric thickness as determined by the (capacitance–voltage (*C*–*V*) measurement. It is found that samples with nitridation of poly-1 have higher breakdown fields (*E*<sub>bd</sub>) than control samples (as deposited). They exhibit a lower leakage current and start conducting at higher voltages than control samples. It is also noted in Fig. 1 that samples with the RTA N<sub>2</sub>O-treatment on poly-1 exhibit an improved *E*<sub>bd</sub> and reduced leakage current. Since the NH<sub>3</sub>-nitridation will introduce hydrogen into the polysilicon, leading to unstable Si-H bonds. The NH<sub>3</sub>-nitridation of poly-1 only moderately improves the dielectric strength. With an additional RTA N<sub>2</sub>O-treatment, the unstable Si-H bonds will be annealed out, resulting in the better electrical characteristics with respect to the NH<sub>3</sub>-treated samples, as shown in Fig. 1. Secondary ion mass spectroscopy (SIMS) measurements of two samples fabricated with and without nitridation of poly-1 are shown in Fig. 2. The profiles of Si+N within the dielectric film are significantly increased by the nitridation treatment. In comparison with the control sample, a relatively high peak of Si+N profile within the dielectric film was observed for the (NH<sub>3</sub>+RTA N<sub>2</sub>O)-nitrided sample. It has been well recognized that the quality improvement of dielectrics by nitridation is thought to be the replacement of strained Si-O bonds or dangling bonds by Si-N bonds, leading to a relaxation of the interface stress [19], [25], [32]. In addition, annealing of dielectric in N<sub>2</sub>O ambient has been used to achieve an oxidation

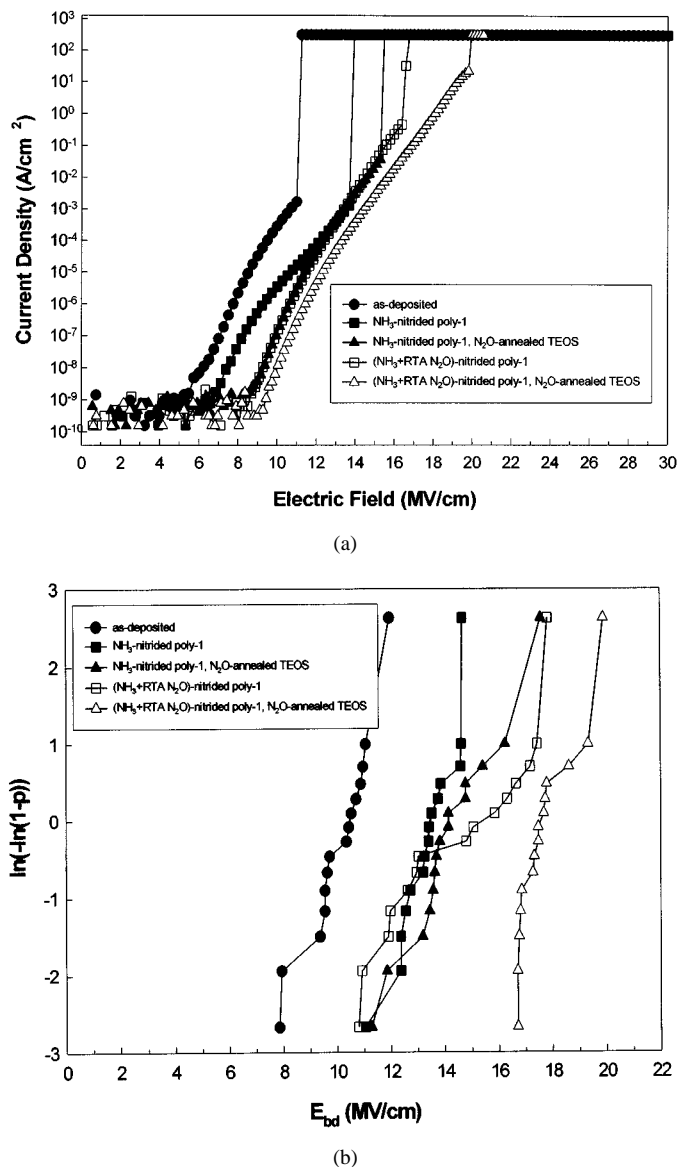


Fig. 1. (a) Typical J-E characteristics of interpoly dielectric layers with or without NH<sub>3</sub> and RTA N<sub>2</sub>O nitridation of poly-1 and N<sub>2</sub>O densification of TEOS under positive applied voltages, i.e., electrons are being injected from the bottom electrode. (b) Typical Weibull distribution of the electrical breakdown field for the as-deposited, deposited on the nitrided-poly-1, and postdeposition annealing interdielectrics.

of the bulk nonstoichiometric SiO<sub>2</sub>, a nitridation at the Si-SiO<sub>2</sub> interface and a densification of the dielectric [19]. Hence, a very high *E*<sub>bd</sub> up to 17 MV/cm (average of 50%) was achieved for the sample by using the (NH<sub>3</sub>+RTA N<sub>2</sub>O)-nitridation of poly-1 and the N<sub>2</sub>O-densification of poly-1.

Plotting the J-E characteristics in the form of a Fowler-Nordheim (F-N) plot (*J*/*E*<sup>2</sup> versus 1/*E*) [30], [31], straight lines were obtained for all samples as shown in Fig. 3, indicating that F-N tunneling is the major conducting mechanism. The transport of F-N tunneling has the form *J* = *C*<sub>1</sub>*E*<sup>2</sup> exp(-*φ*<sub>B</sub>/*E*), where *E* is the field, and *C*<sub>1</sub> and *φ*<sub>B</sub> are constants in terms of effective mass and barrier height. Indeed, the barrier height increased upon nitridation of poly-1, and N<sub>2</sub>O densification of TEOS. In all fabrication conditions, samples with (NH<sub>3</sub>+RTA N<sub>2</sub>O) nitridation of poly-1 and N<sub>2</sub>O-densification of TEOS has

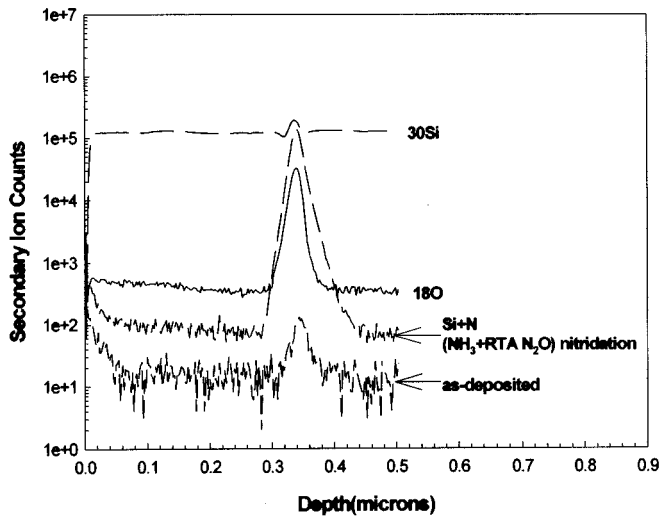


Fig. 2. SIMS profile of two samples fabricated with  $(\text{NH}_3 + \text{RTA } \text{N}_2\text{O})$  and without nitridation of poly-1.

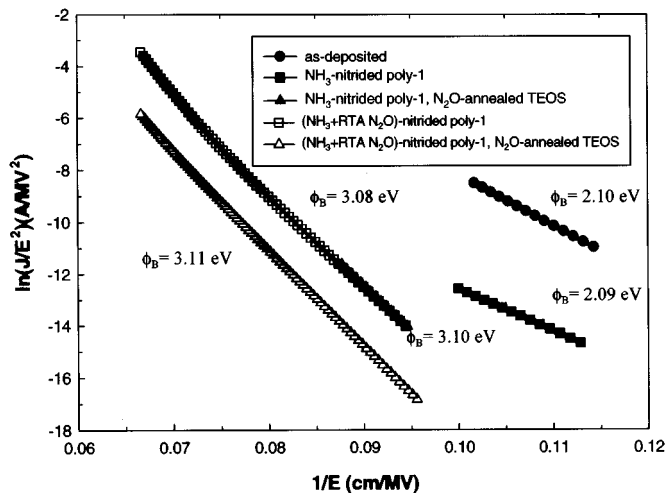


Fig. 3. J-E characteristics in the form of a Fowler-Nordheim plot ( $J/E^2$  versus  $1/E$ ) for all dielectric layers. According to the F-N model, from the corresponding slopes of these lines the barrier heights for the electron were obtained.

the highest effective electron barrier height. Fig. 4 displays the surface images of the poly-1 film with or without nitridation of poly-1 and  $\text{N}_2\text{O}$ -densification of TEOS by the atomic force microscope (AFM) measurement. The surface morphology of the poly-1 without/with the nitridation, and RTA  $\text{N}_2\text{O}$ -densification of TEOS are shown in Fig. 4(a)–(c). Root mean square (RMS) roughness for these three samples are 97.8, 85.6, and 71.8 Å, respectively. This implies  $\text{NH}_3$  and RTA  $\text{N}_2\text{O}$ -nitridation results in a smooth surface. The dielectrics deposited on the  $(\text{NH}_3 + \text{RTA } \text{N}_2\text{O})$ -nitrided poly-1 and  $\text{N}_2\text{O}$ -densification of TEOS exhibit the smoothest interface and hence result in the higher breakdown field.

Fig. 5 shows shift of gate-voltage under the constant current stressing at  $100 \mu\text{A}/\text{cm}^2$  for all capacitors. It reveals that the additional RTA  $\text{N}_2\text{O}$ -nitridation of poly-1 has a smaller voltage shift than the  $\text{NH}_3$  nitrided-only sample. This implies that samples with the additional RTA  $\text{N}_2\text{O}$ -nitridation of poly-1

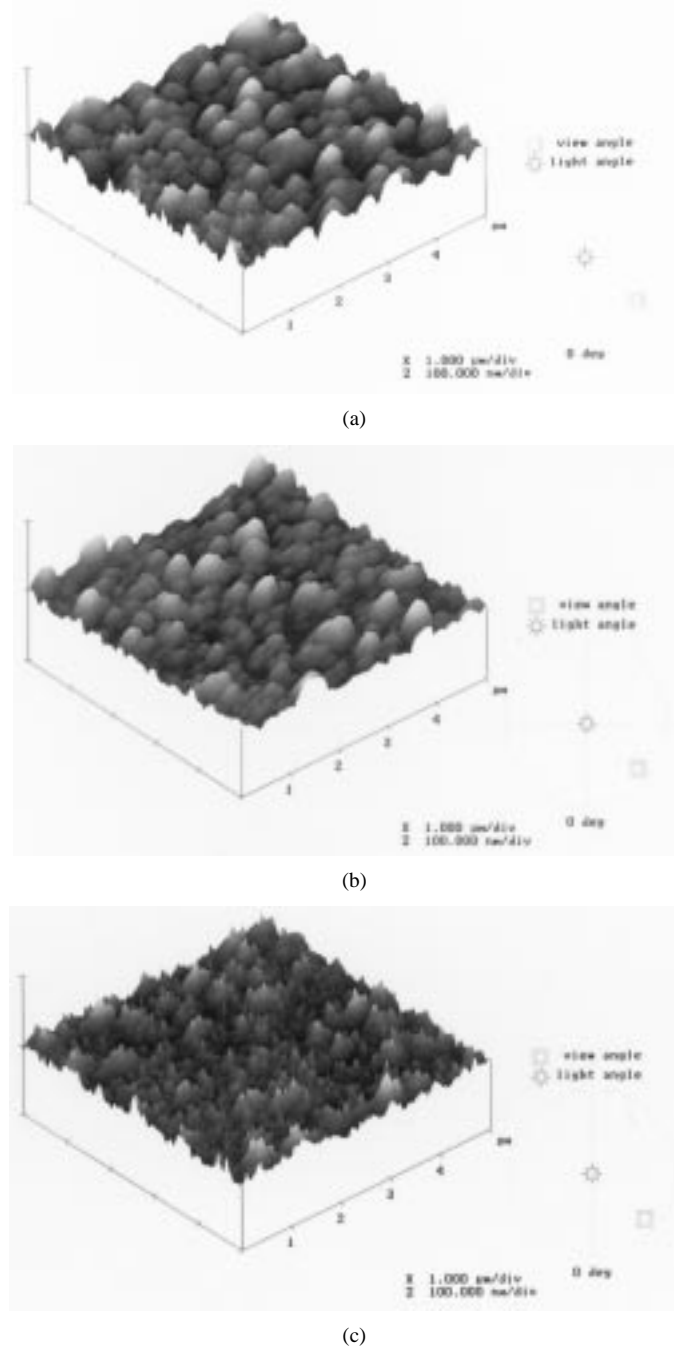


Fig. 4. Surface images of the polysilicon film by AFM measurement. (a) As-deposited, (b)  $\text{NH}_3$ -nitrided poly-1, and (c)  $\text{NH}_3$  and RTA  $\text{N}_2\text{O}$ -nitrided poly-1 with additional  $\text{N}_2\text{O}$  densification of TEOS.

yield a better immunity to the trapping of charges. Relatively, the rougher dielectric/poly-1 interface leads to a smaller conduction area and a higher local current density, subsequently causing a higher trapping rate of charge [23]. For the sample of  $(\text{NH}_3 + \text{RTA } \text{N}_2\text{O})$ -nitrided poly-1 and  $\text{N}_2\text{O}$ -densification of TEOS, a small initial hole trapping is found, after that, no significant trapping is observed. This is due to the highest nitrogen incorporation among these samples.

Regarding the reliability of polyoxide in nonvolatile memories, charge-to-breakdown ( $Q_{\text{bd}}$ ) is also a critical parameter of interest. Dielectrics with large value of  $Q_{\text{bd}}$  are needed to guarantee long read/write cycles. In the conventional polyoxide fab-

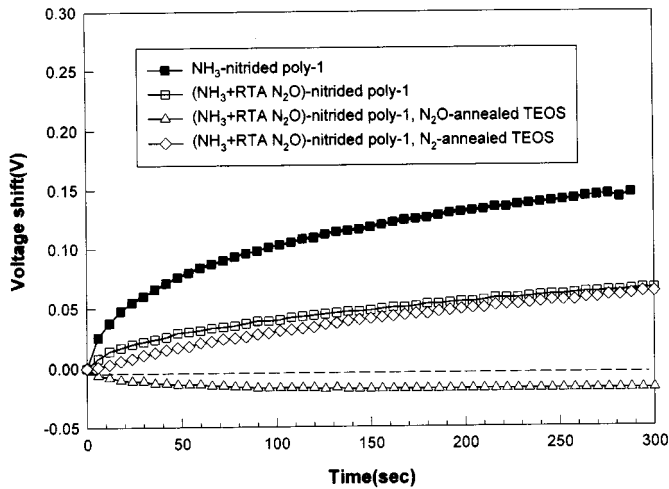


Fig. 5. Charge trapping characteristics, i.e., curves of gate voltage shifts versus stress time under positive top bias with a constant current stressing at  $100 \mu\text{A}/\text{cm}^2$ .

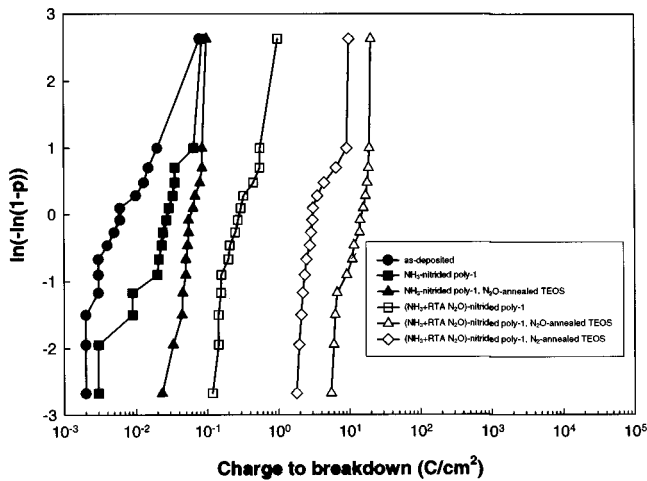


Fig. 6. Typical Weibull plots of the charge-to-breakdown for the as-deposited, nitrided-poly-1, and postdeposition annealed interdielectric layers under positive stress.

rication,  $Q_{\text{bd}}$  values are very small (in the range of  $0.01 \text{ }^\circ\text{C}/\text{cm}^2$  to  $0.1 \text{ }^\circ\text{C}/\text{cm}^2$ ) due to surface roughness and nonuniform poly-oxide thickness. In Fig. 6, the Weibull distributions of charge-to-breakdown of 90-capacitor ( $100 \times 100 \mu\text{m}^2$ ) are shown for positive bias at top-gate. In the measurement, a constant current of  $1 \text{ mA}/\text{cm}^2$  was used to stress the control and  $\text{NH}_3$ -nitrided samples (solid symbols) and a constant current of  $100 \text{ mA}/\text{cm}^2$  was stressed for the RTA  $\text{N}_2\text{O}$ -nitrided samples (empty symbols). It is seen that the  $\text{NH}_3$ -nitridation of poly-1 improves dielectric layer slightly, while the additional RTA  $\text{N}_2\text{O}$ -nitridation of poly-1 increases  $Q_{\text{bd}}$  significantly. It can be seen in Fig. 6 that the improvement of  $Q_{\text{bd}}$  is about from  $0.01 \text{ C}/\text{cm}^2$  to  $0.1 \text{ C}/\text{cm}^2$  by using  $\text{NH}_3$ -nitridation only. This may be due to the incorporation of hydrogen atoms at the dielectric/poly-1 interface. But if the poly-1 was nitrided with the additional RTA  $\text{N}_2\text{O}$ ,  $Q_{\text{bd}}$  increases significantly. In addition to the improvement on roughness of poly-1 as discussed in Fig. 4, the improved integrity is also due to the incorporation of nitrogen atoms, which reduce

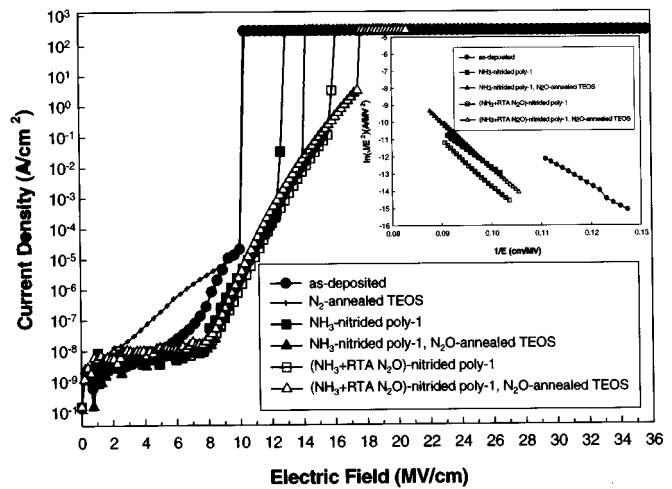


Fig. 7. Typical J-E characteristics of interpoly dielectric layers with or without  $\text{NH}_3$  and RTA  $\text{N}_2\text{O}$  nitridation of poly-1 and  $\text{N}_2\text{O}$  densification of TEOS under negative applied voltages, i.e., electrons are being injected from the top electrode. The inset is a Fowler-Nordheim plot ( $J/E^2$  versus  $1/E$ ) under negative top bias.

the weak Si-O (Si-H) bonds and relax the interface stress [19], [25]. Again, it is seen that a densification of TEOS by  $\text{N}_2\text{O}$  (or  $\text{N}_2$ ) annealing can further improve the dielectric integrity. It is found that  $Q_{\text{bd}}$  up to  $20 \text{ C}/\text{cm}^2$  can be obtained as the poly-1 was nitrided by the  $\text{NH}_3$  and RTA  $\text{N}_2\text{O}$ -annealing and the TEOS annealed with  $\text{N}_2\text{O}$  postdeposition.

So far, only the electron injection from the bottom electrode has been considered. For the negative top electrode bias, i.e., electron injection from the top electrode, it had been shown that dielectrics with an additional  $\text{N}_2\text{O}$  postannealing conducted a higher current than the as-deposited oxides [19], which is in contrast to positive top bias. This polarity preference was also observed for interdielectric layers directly grown from  $\text{N}_2\text{O}$  [25]. Fig. 7 shows the J-E characteristics for the samples under negative bias at top-gate. Although the postdeposition annealing results in the polarity asymmetry, it is found that samples with nitridation of poly-1 still exhibit a better performance than the as-deposited samples. As compared to Fig. 1, the leakage currents of negative bias are one order of magnitude higher than those obtained from the positive bias. This is mainly ascribed to the nitrogen incorporated at the interdielectric/poly-1 interface. The inset in Fig. 7 depicts the F-N plots for electron injection from the top gate. Although the barrier height for the electron tunneling from poly-2 to the  $\text{SiO}_2$  is not strongly related to the nitridation of poly-1 and the densification of TEOS, it is found that the barrier height is slightly improved with nitridation and  $\text{N}_2\text{O}$  densification of TEOS as shown in Fig. 7. The Weibull distributions of  $Q_{\text{bd}}$  under the negative bias are shown in Fig. 8. It is noted that the improvements of  $Q_{\text{bd}}$  using nitridation of poly-1 and densification of TEOS are similar to the positive top gate bias. The inset of Fig. 8 shows the charge trapping characteristics under constant current stressing at  $100 (\mu\text{A}/\text{cm}^2$  for the negative bias at top-gate. The shift of gate-voltage increases with time. The additional RTA  $\text{N}_2\text{O}$ -nitridation of poly-1 has a smaller voltage shift than the  $\text{NH}_3$ -nitrided capacitor. This finding also implies that the additional RTA  $\text{N}_2\text{O}$ -nitridation of

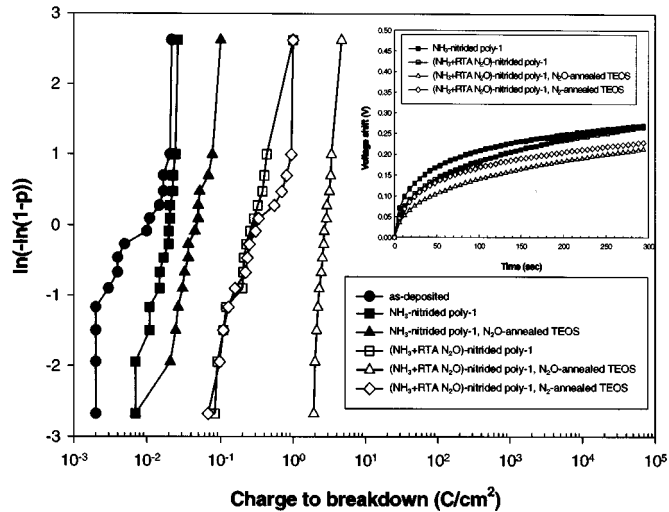


Fig. 8. Typical Weibull plots of the charge-to-breakdown for the as-deposited, nitrided-poly-1, and postdeposition annealed interdielectric layers under positive stress. The inset is the charge trapping characteristics under negative top bias.

poly-1 yields a better immunity to electron trapping, no matter what directions of electrons are injected. Furthermore, as TEOS was annealed in  $N_2O$  ambient, the sample exhibits a better performance of charge trapping characteristic, which results in a higher charge-to-breakdown as seen in Fig. 8. However, as compared to Fig. 5, the electron trapping rates of capacitors under the negative bias at top gate are higher than those obtained from the positive bias counterpart. This is due to the different position of trapped charges in the  $N_2O$ -annealed oxide under different gate bias, which is similar to the physical model proposed in [4].

#### IV. CONCLUSION

In this study, an  $NH_3$  with RTA  $N_2O$  process to incorporate nitrogen at dielectric/polysilicon interface has demonstrated to improve integrity of polyoxides. Polyoxides deposited on this nitrided polysilicon with the additional  $N_2O$ -densification exhibit a lower leakage current, higher electric breakdown field, higher electron barrier height, lower electron trapping rate, and much higher charge-to-breakdown than the as-deposited polyoxides. SIMS results show the incorporation of nitrogen at the polyoxide/poly-1 interface, which improves electrical properties in return. Polyoxides formed by this method can achieve a high breakdown field up to 17 MV/cm and charge-to-breakdown more than  $20\text{ }^\circ\text{C}/\text{cm}^2$ . This process appears to be a very attractive alternative for conventional polyoxides.

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