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PAPER *Special Issue on Sub-1/4 Micron Device and Process Technologies*

Thickness Dependence of Furnace N_2O-Oxynitridation Effects on Breakdown of Thermal Oxides

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SUMMARY Thickness dependence of breakdown properties in control and N_2O-oxynitrided oxides was investigated. Nitrogen atoms piled up at the Si/SiO_2 interface increase charge-to-breakdown (Q_{BD}) under substrate injection conditions for oxide thickness below 10 nm, while no meaningful improvement is observed above 10 nm. This thickness dependence is explained by the fact that N_2O-oxynitridation reduces oxide defects near the Si/SiO_2 interface. N_2O-oxynitridation of the oxides reduces the number of neutral electron traps due to the chemical reaction of oxide defect with nitrogen atoms. Electron trapping of N_2O-oxynitrided oxides is significantly suppressed; the reduction of electron trapping events into neutral electron traps increases Q_{BD} under substrate injection. On the other hand, under gate injection, N_2O-oxynitrided oxides show low rate of hole trapping during the initial stress period. However, in heavily injected condition, electron trapping is not suppressed, resulting in little improvement of Q_{BD}. In addition, the control and N_2O-oxynitrided oxides show quite similar dependence of Q_{BD} on stress current density, which is related primarily to the carrier transport phenomena (tunneling, traveling, impact ionization and hole injection).

key words: *N_2O-oxynitridation, charge-to-breakdown, thin dielectrics, MOS structure, dielectric reliability*

1. Introduction

For the past decade, considerable works on oxynitrides [1]–[11] have been reported as alternative gate dielectrics for deep submicrometer MOS devices. The high reliability of oxynitrides originates from rigid Si–N bonds at the Si/SiO_2 interface [3]–[5], [11], [12]. It has been reported that N_2O-based oxidation process is more promising than NH_3-nitridation of SiO_2 due to the hydrogen-free nature of the processing [4]. Incorporation of hydrogen in gate oxide during NH_3-nitridation requires light nitridation and/or an additional reoxidation or N_2 annealing with rapid thermal processing (RTP) to reduce electron traps in nitrided oxides [8], [11]. Simultaneous oxidation and nitridation occurred during N_2O-oxynitridation result in the increase of the oxide thickness and the decrease of the oxide defect density.

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N_2O-oxynitridation processing is classified into two categories such as resistance-heated furnace processing and RTP. Although RTP is a promising alternative to a conventional resistance-heated furnace, the latter is still the dominant process equipment in today's LSI fabrication lines. Chu et al. showed that N_2O-oxynitrides grown by RTP exhibit both thickness and compositional nonuniformities [13] though the process controllability and dielectric integrity of N_2O-based dielectrics are important issues. In addition, the growth of oxynitrides in pure N_2O ambient requires unacceptable long oxynitridation time because the oxynitridation in N_2O ambient shows significantly lower growth rate. Therefore, the conventional thermal oxidation followed by furnace N_2O-oxynitridation is a promising process [6], [9].

Ahn et al. reported that the furnace N_2O-oxynitrided oxides show higher endurance in time-to-breakdown under substrate electron injection compared to those of control oxides with the thickness of 8.5 nm [6]. Joshi et al. reported the breakdown properties of oxynitrides grown directly in N_2O ambient with thickness range from 4.7 to 12 nm [10]. However, no literatures have been reported on the thickness dependence of the breakdown properties of oxynitrides formed by the furnace N_2O-oxynitridation of the conventional thermal oxides.

In this study, we have investigated the breakdown properties of the N_2O-oxynitrided oxides with various thicknesses formed by the furnace processing. The aim of this study is to clarify mechanisms of improvement of breakdown properties in N_2O-oxynitrided oxides.

2. Sample Preparation

The samples used in this study were MOS capacitors with n^+ and p^+ poly-Si gate electrodes fabricated on p and n-type (100)-oriented Si wafers, respectively. The capacitors were isolated using standard LOCOS process. Electrons are injected into the gate oxides using constant Fowler-Nordheim (F-N) tunneling current stress method. In the above two sample structures, the total energy losses of the injected electrons are quite similar [14], meaning that carrier transport in the two

structures are similar regardless of the oxide field polarity.

The wafers were oxidized at 800°C in dry O_2/HCl ambient. Some of the wafers were followed by the oxynitridation of the control oxides at 950°C for 20 min in N_2O ambient to form N_2O-oxynitrided oxides. During the N_2O-oxynitridation process, oxide thickness increases about 2 nm regardless of pure oxide thickness. This indicates that the oxynitridation process is limited by the chemical reaction at the Si/SiO_2 interface. After the gate oxidation, a poly-Si gate with 150-nm thickness was deposited by low-pressure chemical-vapor-deposition (LPCVD). The n^+ and p^+ poly-Si gate electrodes were doped by phosphorus diffusion and boron ion implantation, respectively. The boron ion implantation ($^{11}B^+$, 15 keV, 3×10^{15} cm^{-2}) was implemented after silicon ion implantation for an amorphous layer formation. After delineating the gate electrodes by optical lithography and reactive ion etching, the wafers were annealed at 900°C for 10 min in N_2 ambient. The capacitor area used was 0.44 mm^2. The oxide thickness was measured with a well-calibrated automatic ellipsometer with the refractive index of 1.46, and was evaluated after averaging five measurements within an area of the wafer.

Using high-frequency C-V measurements, we confirmed that boron penetration was suppressed sufficiently for p^+ poly-Si gate samples in this process. This is due to the fact that boron ions are implanted into the oxides without fluorine incorporation [15]. In addition, using quasi-static C-V measurements, we also confirmed that the depletion near the poly-Si/SiO_2 interface was suppressed for the p^+ poly-Si gate samples.

3. Results and Discussion

We studied breakdown properties of the control and the N_2O-oxynitrided oxide films under the F-N electron injection from either the gate electrodes (gate injection, $-V_G$) or the substrates (substrate injection, $+V_G$). Figures 1 (a) and 1 (b) show band diagrams under gate injection in n^+ poly-Si gate MOS capacitors and under substrate injection in p^+ poly-Si gate MOS capacitors, respectively.

Figures 2 (a) and 2 (b) show charge-to-breakdown (Q_{BD}) in the control and the N_2O-oxynitrided oxides as a function of oxide thickness (T_{OX}) for the substrate injection in the p^+ poly-Si gate samples and the gate injection in the n^+ poly-Si gate samples, respectively. Figure 2 (a) demonstrates that under the substrate injection for the p^+ poly-Si gate samples, Q_{BD} values in the N_2O-oxynitrided oxides show excellent improvement for thicknesses below 10 nm. Above 10 nm, slight improvement of Q_{BD} values over the control oxides is observed. On the other hand, as is shown in Fig. 2 (b), under the gate injection for n^+ poly-Si gate samples, no meaningful difference between the control and the

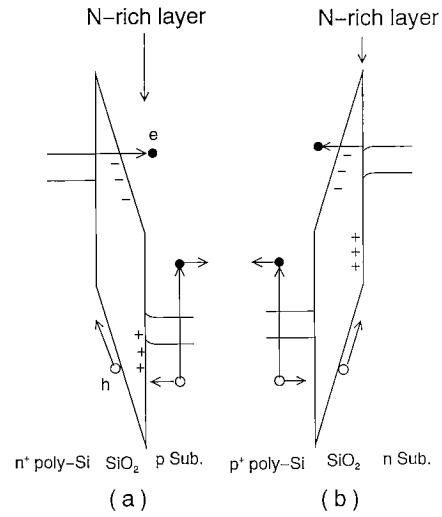

Fig. 1 Energy band diagrams of MOS capacitors (a) under gate injection in n^+ poly-Si gate MOS capacitors and (b) under substrate injection in p^+ poly-Si gate MOS capacitors.

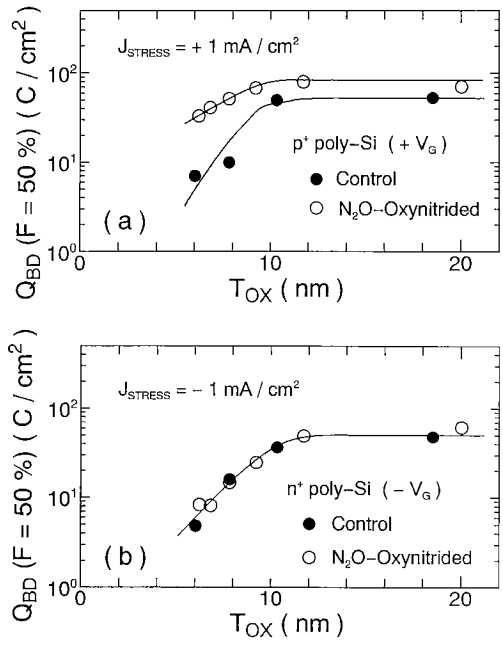

Fig. 2 Oxide thickness (T_{OX}) dependence of charge-to-breakdown (Q_{BD}) for 50% failure (a) under the substrate injection in the p^+ poly-Si gate samples and (b) under the gate injection in the n^+ poly-Si gate samples.

N_2O-oxynitrided oxides is observed in terms of Q_{BD}.

As can be seen in Figs. 2 (a) and 2 (b), the oxide thickness dependences of Q_{BD} in control oxides are similar for the substrate injection and the gate injections. This is attributed to the similar total energy loss of injected electrons between p^+ poly-Si gate samples and n^+ poly-Si gate samples at a constant F-N tunneling current density [14]. Fukuda observed that Q_{BD} in gate injection decreases with decreasing oxide thickness, while increases in substrate injection [16]. One of the

reasons of this discrepancy is that his samples used for substrate injection have n^+ poly-Si gate, resulting in the lower average total energy loss of the injected electrons than that for gate injection in n^+ poly-Si gate samples on p-type wafers.

In addition, Liang and Choi observed that as stress current increases, Q_{BD} behavior with reduction in oxide thickness changes from increasing to decreasing for the both gate and substrate injection [17]. However, we cannot also observed this tendency for $|J_{STRESS}| = 1-100\,mA/cm^2$. The reason is that the capacitor area of our samples ($0.44\,mm^2$) is larger than that of theirs ($1\times10^{-3}\,mm^2$). As described latter, the power exponent, n of $Q_{BD} \propto J_{STRESS}^{-n}$ increases with reduction in oxide thickness. Therefore, thickness dependence of Q_{BD} at a fixed stress current density is thought to be decided by the compensation between the increase of n and the variation of oxide defect number (oxide defect density times capacitor area) with reduction in thickness. If we use lower stress current densities and longer measurement time, the above tendencies may be observed for our samples.

The excellent Q_{BD} improvement below 10 nm under the substrate injection may be caused by thickness dependence of oxide defects: N_2O-oxynitridation reduces the number of oxide defects in the transition layer. No improvement under the gate injection condition is attributed to the fact that electron trapping is not reduced under gate injection, while trapping events into neutral electron trap centers are reduced under substrate injection, as discussed in what follows.

The breakdown properties are associated primarily with the carrier trapping characteristic. To investigate the effect of nitrogen atoms piled up near the Si/SiO_2 interface on carrier trapping behavior, we studied carrier trapping behavior at high oxide field by taking account of the field polarity.

Figures 3 (a) and 3 (b) show the oxide thickness dependence of charge trapping properties under the gate injection for the control and the N_2O-oxynitrided oxides: The figures demonstrate the relative shift of the applied oxide field under a constant F-N tunneling current condition $\Delta V_G/T_{OX}$ as a function of stress time. The thicker control oxides (T_{OX} = 7.8, 10.3 nm) exhibit a small net positive charge trapping during the initial stress period, which is attributed to the existence of hole traps near the Si/SiO_2 interface. The hole trapping strongly depends on T_{OX}: the thinner oxide has lower hole trapping rate. Lo et al. also found similar phenomenon under gate injection for thermal oxides grown by RTP [18]. According to their model, the electrons in thicker oxide without suffering the trapping events gain higher energy from the applied field, which leads to higher rate of hole generation in the oxide bulk through impact ionization. As electron injection from the gate electrode continues, electron trapping becomes dominant in the thicker control oxides as seen

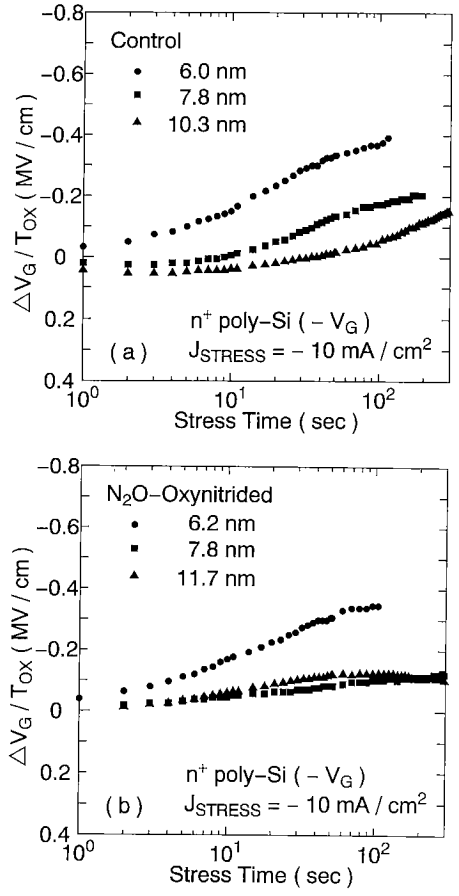

Fig. 3 Stress time dependence of the shift of the applied oxide field $\Delta V_G/T_{OX}$ in the n^+ poly-Si gate samples with (a) the control and (b) the N_2O-oxynitrided oxides as a function of stress time under the gate injection at $-10\,mA/cm^2$.

in Fig. 3 (a). Thinnest oxide (T_{OX} = 6.0 nm) shows a significant electron trapping, which differs from the result of Lo et al. [18] The difference of the gate oxidation methods would be a main reason for the discrepancy. Lo et al. used RTP in dry O_2 ambient, while we used the furnace oxidation in dry O_2/HCl ambient. Fukuda et al. confirmed that a 10 nm-thick oxide grown by RTP is superior to conventional furnace-grown oxides in breakdown and Si/SiO_2 interface characteristics [19]. According to their explanation, the reason is that the RTP oxide is formed at high temperature (> 1000 °C), resulting in an automatically flat Si/SiO_2 interface and improvement in the weak Si–O–Si network. Therefore, electron trapping center density in our samples seems to be higher compared with the sample of Lo et al.

On the other hand, compared with the control oxides, all the N_2O-oxynitrided oxides show little net positive charge trapping as seen in Fig. 3 (b), while similar negative charge trapping behaviors with the control oxides. The negative gate voltage shift is primarily related to the electron trap centers near the poly-Si/SiO_2

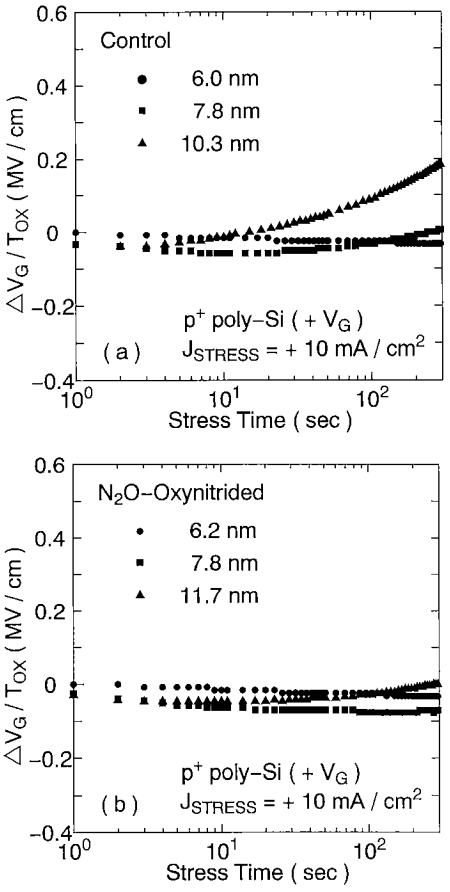

Fig. 4 Stress time dependence of the shift of the applied oxide field $\Delta V_G/T_{OX}$ in the p^+ poly-Si gate samples with (a) the control and (b) the N_2O-oxynitrided oxides as a function of stress time under the substrate injection at $+10$ mA/cm^2.

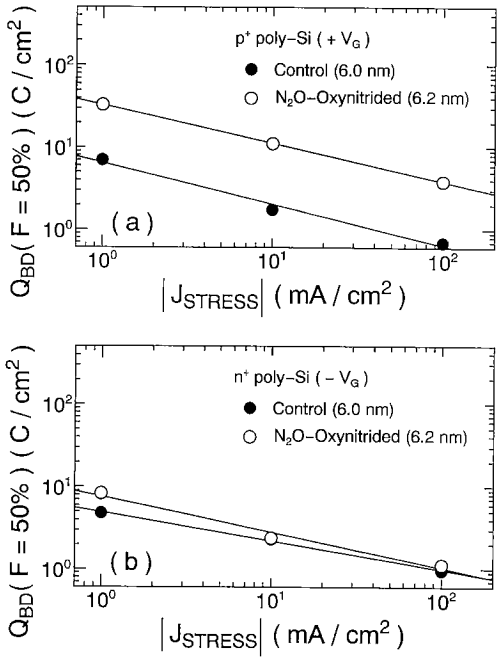

Fig. 5 Charge-to-breakdown (Q_{BD}) as a function of stress current density (J_{STRESS}) (a) under the substrate injection in the p^+ poly-Si gate samples and (b) under the gate injection in the n^+ poly-Si gate samples.

interfaces as seen in Fig. 1 (a). This means that N_2O-oxynitridation has no effect on electron trapping under the gate injection. Reduction of the positive charge trapping by N_2O-oxynitridation is attributed to the decrease of hole trap density due to the existence of nitrogen atoms near the Si/SiO_2 interface. On the basis of the broken bond model [20], trivalent silicon defects Si^* ($O_3 \equiv Si^\bullet$ and/or $Si_3 \equiv Si^\bullet$) play a significant role of hole trap centers such as $O_3 \equiv Si^\bullet + h^+ \rightarrow O_3 \equiv Si^+$. Fukuda et al. pointed out that the trivalent silicon defects Si^* are annihilated after the formation of rigid Si–N bonds near the Si/SiO_2 interface [3].

Figures 4 (a) and 4 (b) show the oxide thickness dependence of the charge trapping properties of the control and the N_2O-oxynitrided oxides under the substrate injection. Figure 4 (a) shows that the thicker control oxides ($T_{OX} = 7.8, 10.3$ nm) exhibit a slight net positive charge trapping during the initial stress period, and then a significant negative charge trapping during the following stress. The thinnest control oxide ($T_{OX} = 6.0$ nm) exhibits a slow positive charge trapping. These experimental results indicate that for the thicker oxides, the hole generation due to high energy electrons and the electron trapping occur simultaneously. Figure 4 (b) shows that the positive charge trapping behavior during the initial stress period seems to have no difference with that of the control oxides. However, it is shown that the electron trapping rate during the following stress is reduced. This behavior differs from that under the gate injection. Uchida et al. pointed out that trapped holes near the Si/SiO_2 interface generate neutral electron traps [21], which originate from the relaxation of strained bonds near the interface due to hole trapping. Since nitrogen incorporation by N_2O-oxynitridation reduces strained bonds near the Si/SiO_2 interface, one can simply expect the reduction of the neutral electron traps in N_2O-oxynitrided oxides.

Figure 5 (a) shows Q_{BD} values of the p^+ poly-Si gate MOS capacitors as a function of stress current J_{STRESS} under the substrate injection condition. The power exponents, n of $Q_{BD} \propto J_{STRESS}^{-n}$ for the control oxides is the same as that of N_2O-oxynitrided oxides. Figure 5 (b) shows Q_{BD} versus current density of the n^+ poly-Si gate capacitors for the gate injection condition. There exists no significant difference between the control and the N_2O-oxynitrided oxides. Figure 6 shows n value as a function of oxide thickness, T_{OX}. The value n increases with decreasing T_{OX}. This is attributed to the effective traveling distance of electrons in the oxides (the oxide thickness minus the tunneling distance) [17]. As the electron traveling distance in the oxides nearly equals to the energy relaxation length, the

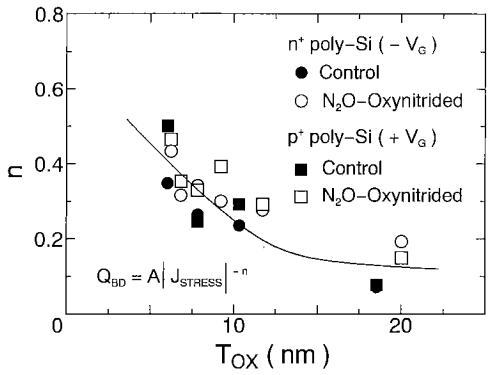

Fig. 6 The power exponent n as a function of oxide thickness (T_{OX}) in the form $Q_{\mathrm{BD}} \propto J_{\mathrm{STRESS}}^{-n}$.

nonstationary electron transport in the oxides becomes significant, resulting in the large dependence of the electron energy on the traveling distance. The traveling distance increases with increasing the oxide field due to the decrease of the tunneling distance. This results in the large influence of the oxide field on the breakdown. Scarce dependence of the stress current polarity on n reflects the similarity of the average energy of the injected electrons between p^+ poly-Si gate and n^+ poly-Si gate MOS capacitors at constant F-N tunneling current densities [14]. The power exponent n is directly related to the physical mechanisms of carrier transport in the oxides; tunneling, traveling, impact ionization and hole injection, as shown in Figs. 1 (a) and (b).

4. Conclusions

We have investigated thickness dependence of breakdown properties in the control and the N_2O-oxynitrided oxides. Nitrogen atoms piled up at the Si/SiO_2 interface increases Q_{BD} under substrates injection for oxide thickness below 10 nm, while only slight increase is observed for the oxide above 10 nm. This thickness dependence is explained by the fact that N_2O-oxynitridation reduces oxide defects whose fraction is larger in thinner control oxides due to the existence of the transition layer. Under heavily injected condition from the substrate, the rate of electron trapping into neutral electron traps is smaller for the N_2O-oxynitrided oxides than for the control oxides. The dynamical carrier trapping behaviors reflect the breakdown properties; the reduction of electron trapping centers near the Si/SiO_2 interface after N_2O-oxynitridation increases Q_{BD} under substrate injection. On the other hand, under gate injection condition, N_2O-oxynitrided oxides show the reduction of hole trapping during the initial stress period but no meaningful difference on electron trapping in heavily injected conditions. This results in little improvement on Q_{BD}. In addition, the control and the N_2O-oxynitrided oxides show quite similar dependence of Q_{BD} on stress current density, which is related primarily to the carrier transport phenomena (tunneling, traveling, impact ionization and hole injection).

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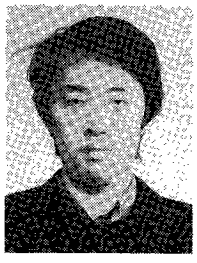

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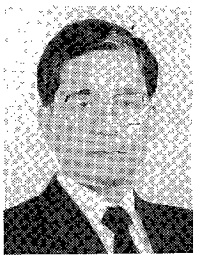

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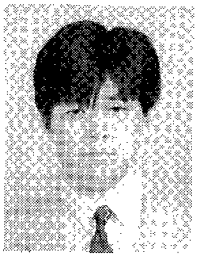

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