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# Electrical Properties of Different NO-Annealed Oxynitrides

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**Abstract** - Performances of gate dielectrics prepared by double nitridation in NO and N<sub>2</sub>O are investigated. Stronger oxide/Si interface, less charge trapping and larger charge-to-breakdown are observed for such gate dielectrics than singly NO-nitrided gate dielectric. The physical mechanisms behind the findings are attributed to larger nitrogen peak concentration located almost at the oxide/Si interface and total nitrogen content near the oxide/Si interface of these gate dielectrics.

## 1. Introduction

As an alternative gate dielectric, oxynitrides have drawn considerable attention due to their superior performance and reliability properties over conventional SiO<sub>2</sub> [1-5]. However, NH<sub>3</sub>-nitrided oxides suffer from hydrogen-related electron trapping problems [2-3] while N<sub>2</sub>O-based oxides require a much larger thermal budget for sufficient nitrogen incorporation [6-7]. To avoid these disadvantages of NH<sub>3</sub> and N<sub>2</sub>O, nitric oxide (NO) has been proposed as a dielectric growth/anneal ambient to obtain better quality dielectric films [8-10]. Furthermore, NO-annealed process (an initial oxide grown in pure oxygen and then annealed in NO ambient) is preferred to prepare oxynitride with sufficient thickness in a reasonable time for manufacturing purposes, considering self-limiting of the growth process in NO ambient. This investigation further finds that NO nitridation combined with N<sub>2</sub>O nitridation (i.e. double nitridation) is a promising technique. In detail, if the initial oxide is grown in N<sub>2</sub>O and then annealed in NO ambient, or the initial oxide is grown in O<sub>2</sub> and then nitrided in NO ambient followed by N<sub>2</sub>O annealing, better dielectric films with a harder oxide/Si interface, less charge trapping, and larger breakdown fields can be obtained compared with these properties in singly NO-nitrided dielectric films. We attribute the involved mechanisms to larger interfacial nitrogen concentration and total nitrogen content in the double-nitridation oxynitrides. This work reports relevant results in terms of stress-induced increase of interface-state density and shift of flat-band voltage, and charge trapping and breakdown properties of MOS capacitors.

## 2. Experimental

MOS capacitors were fabricated on p-type (100) silicon wafers with a resistivity of  $\sim 7 \Omega\text{-cm}$  by a self-aligned n<sup>+</sup> polysilicon gate process. Gate oxides were grown in a conventional horizontal furnace in either dry O<sub>2</sub> or pure N<sub>2</sub>O ambient at 950 °C to the same thickness of 7.0 nm (NO was not used due to its low oxidation rate). They were then annealed in a pure

NO ambient at 950 °C for 30 min (denoted as ONO for O<sub>2</sub> growth and N2ONO for N<sub>2</sub>O growth) to increase their nitrogen contents. Some of the ONO samples were further annealed in N<sub>2</sub>O ambient at 950 °C for 30 min (denoted as ONON2O) to provide another form of doubly-nitrided sample for comparing with N2ONO sample. Final oxide thickness measured by a capacitance voltage (C-V) technique was  $8.2 \pm 0.5$  nm for ONO sample,  $7.4 \pm 0.5$  nm for N2ONO sample and  $9.3 \pm 0.5$  nm for ONON2O sample. Control sample with a film thickness of  $8.5 \pm 0.5$  nm was thermally grown also at 950 °C in dry O<sub>2</sub> (denoted as OX). All gate oxides finally received an *in situ* N<sub>2</sub> anneal at 950 °C for 20 min. To study the interface and charge-trapping properties, Fowler-Nordheim (F-N) constant-current stress was used with electron injection from the gate, and the oxide/Si interface as the collecting electrode and the site of greatest damage. Increase in mid-gap interface-state density ( $\Delta D_{itm}$ ), shift of flat-band voltage ( $\Delta V_{fb}$ ), charge-to-breakdown (Q<sub>BD</sub>), and change in gate voltage ( $\Delta V_G$ ) were measured on the MOS capacitors with an area of  $10^{-4}$  cm<sup>2</sup>. All measurements were carried out in a light-tight and electrically-shielded environment.

### 3. Results

#### 3.1 Nitrogen profile

The nitrogen profiles of the three oxynitrides were studied by secondary ion mass spectroscopy (SIMS) technique using Cs<sup>+</sup> bombardment and CsN<sup>+</sup> detection, and shown in Fig. 1. Two important points can be extracted: 1) N2ONO and ONO oxynitrides have the largest and smallest peak nitrogen concentrations (N<sub>p</sub>), respectively, with N<sub>p</sub> of ONON2O oxynitride close to that of N2ONO oxynitride; 2) the location of N<sub>p</sub> is almost at the interface in the N2ONO and ONON2O samples, while it is inside the Si substrate in the case of the ONO sample. Thus the total nitrogen contents in the two doubly-nitrided samples are larger than that in the singly-nitrided sample because their nitrogen profiles have almost identical

width at half of  $N_p$  (3.0 nm for N2ONO oxynitride, 3.2 nm for ONO oxynitride and 3.4 nm for ONON2O oxynitride).

### 3.2 Device properties

The hardness of the oxide/Si interface is evaluated by  $\Delta D_{itm}$  of the capacitors after a F-N constant-current stress at  $-10 \text{ mA/cm}^2$  (the substrate as anode) for different injection times. As shown in Fig. 2, the creation of oxide/Si interface states of the three nitrated samples is suppressed as compared to OX sample due to interfacial nitrogen incorporation, with N2ONO sample better than the other two nitrated samples owing to its larger  $N_p$  at the oxide/Si interface. This difference indicates that a double nitridation by NO and  $N_2O$  can result in a harder oxide/Si interface than a single NO nitridation because more nitrogen incorporation at/near the oxide/Si interface, as shown in Fig.1, can produce more strong Si-N and N-O bonds.

Electron trapping in the oxide were examined by monitoring the change in gate voltage of the capacitors to maintain a constant current density of  $10 \text{ mA/cm}^2$  with gate injection. As shown in Fig. 3, the electron trapping of ONON2O oxynitride is smaller than that of ONO oxynitride, while the opposite holds for the other doubly-nitrated sample N2ONO.

Fig. 4 is the flat-band voltage shift of the capacitors under the same F-N stress conditions as those in Fig. 2. Again, N2ONO sample is most resistant to the hot-carrier stress and poorer resistance is observed in the ONON2O sample. A negative shift in  $V_{fb}$  indicates hole trapping, which is maybe due to generated donor-like interface states [11] and bulk trapping near the oxide/Si interface. We assume that creation of hole traps at/near the oxide/Si interface is more effectively suppressed for the two doubly-nitrated samples (N2ONO and ONON2O) than in the case of ONO oxynitrides due to more nitrogen incorporation near the interface.

Presented in Fig. 5 is the charge-to-breakdown of the gate oxides under a constant-current stress of  $-100 \text{ mA/cm}^2$ . Improved  $Q_{\text{BD}}$  of oxynitrides is obtained as compared to thermal oxide (OX), with ONON2O oxynitride the best due to its suppressed electron-trap generation/trapping.

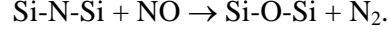
## 4. Discussions

### 4.1 Nitrogen profile

For N2ONO and ONON2O oxynitrides, the larger  $N_p$  is due to additional incorporation of nitrogen during the  $\text{N}_2\text{O}$  oxidation and annealing. Their  $N_p$ 's locations are determined by the combined effect of  $\text{N}_2\text{O}$  and NO nitridations, because  $N_p$  of  $\text{N}_2\text{O}$  nitridation is inside the oxide while that of NO nitridation is inside the Si substrate [10]. Therefore, the double nitridation by NO and  $\text{N}_2\text{O}$  is favourable in adjusting the location of  $N_p$  to the oxide/Si interface, as well as increasing the interfacial nitrogen incorporation. Additionally, the smaller thickness increase of N2ONO oxynitride (0.4 nm) than that of ONO oxynitride (1.2 nm) after NO annealing implies that better oxidation resistance and thus thickness control can be obtained when the initial oxide is grown in a  $\text{N}_2\text{O}$  ambient. On the other hand,  $\text{N}_2\text{O}$  annealing of ONO sample also produces a thickness increase of 1.1 nm, indicating different kinetics between  $\text{N}_2\text{O}$  and NO annealings.

### 4.2 Device properties

Poorer electron trapping properties of N2ONO oxynitride than ONON2O and ONO oxynitrides is associated with more nitrogen in the interior of N2ONO oxynitride than ONON2O and ONO oxynitrides, as shown in Fig. 1, because interior nitrogen degrades the breakdown, which is related to electron trapping [12, 13], of oxynitrides. The larger amount of interior nitrogen in N2ONO oxynitride comes from the  $\text{N}_2\text{O}$  oxidation, which results in nitrogen incorporation throughout almost the whole oxide [12]. Fortunately, the interior nitrogen can be reduced by NO annealing. A possible reaction [14] for this reduction is



As demonstrated in Fig. 1c, nitrogen concentration is smaller in a large portion of N2ONO sample after the NO annealing. We expect that if the conditions of the NO annealing are optimized, the remaining interior nitrogen can become negligible.

In Fig. 5, the extent of  $Q_{\text{BD}}$  gain for the three oxynitrides basically follows that of their  $\Delta V_g$  reduction shown in Fig. 3, implying that the breakdown is related to electron trapping in the oxides. In other words, the larger the electron-trap generation/trapping rate, which is proportional to the slope of  $\Delta V_G$  versus injected charge in Fig. 3, the smaller is  $Q_{\text{BD}}$  [13, 15]. On the other hand, we assume that the oxide/Si interface properties would also affect the breakdown of devices, because it is found that more trap generation at the interface is accompanied by a smaller  $Q_{\text{BD}}$  [16]. Therefore, we suggest that  $Q_{\text{BD}}$  is controlled by a combined effect of electron trapping in oxide and interface-trap generation, with the former probably dominant. This effect is why N2ONO sample has a  $Q_{\text{BD}}$  almost identical to ONO sample, although the former has more electron trapping but less  $\Delta D_{\text{itm}}$  than the latter. Thus, we propose that a sufficiently large amount of N near the oxide/Si interface of oxynitride is effective in suppressing charge trapping and interface degrading, resulting in larger breakdown fields.

## 5. Conclusions

Gate dielectrics with increased resistance against hot-carrier bombardments, suppressed charge trapping and larger breakdown fields can be achieved by double-nitridation processes using both NO and N<sub>2</sub>O. The effects are due to larger interfacial nitrogen concentrations and larger total nitrogen content near the oxide/Si interface of such oxynitrides. Therefore, the double nitridation in NO and N<sub>2</sub>O could be a promising process for preparing gate dielectric in MOS devices.

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**Captions:**

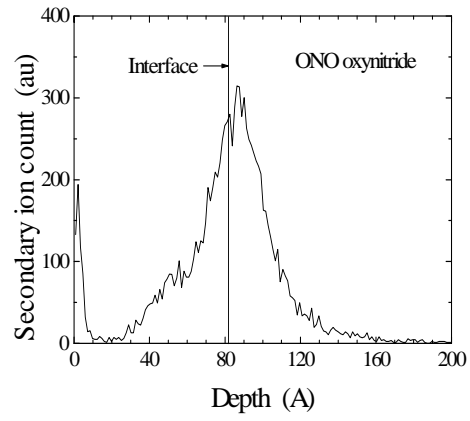
**Fig. 1** SIMS profile of nitrogen for the three oxynitrides. (a) ONO oxynitride, (b) ONON2O oxynitride and (c) N2ONO oxynitride.

**Fig. 2** Increase in midgap interface-state density  $\Delta D_{\text{itm}}$  of MOS capacitors with different gate dielectrics under a constant-current stress of  $-10 \text{ mA/cm}^2$ . Lines are drawn as guides for the eyes.

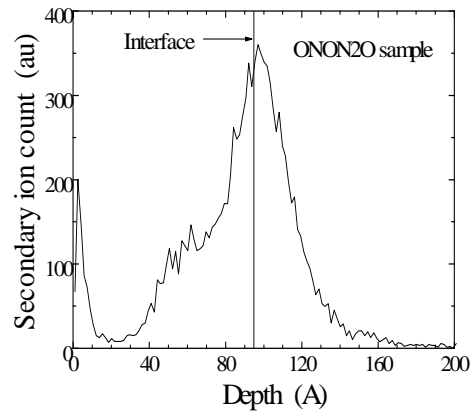
**Fig. 3** Change in gate voltage  $\Delta V_G$  of MOS capacitors under a constant-current stress at  $10 \text{ mA/cm}^2$  with gate injection.

**Fig. 4** Flat-band voltage shift  $\Delta V_{\text{fb}}$  of MOS capacitors under the same stress conditions as those in Fig. 2. Lines are drawn as guides for the eyes.

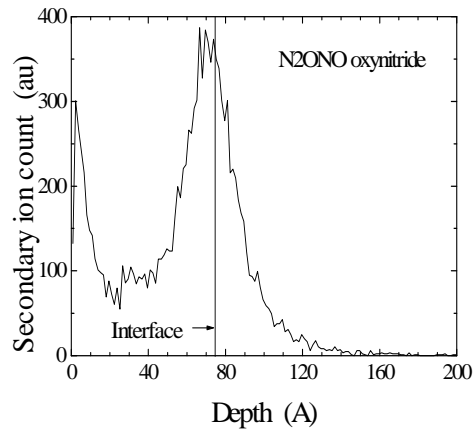
**Fig. 5** Charge-to-breakdown  $Q_{\text{BD}}$  of gate dielectrics measured under a constant-current stress at  $100 \text{ mA/cm}^2$  with gate injection. The line is drawn as a guide for the eyes.



(a)



(b)



(c)

**Fig. 1**

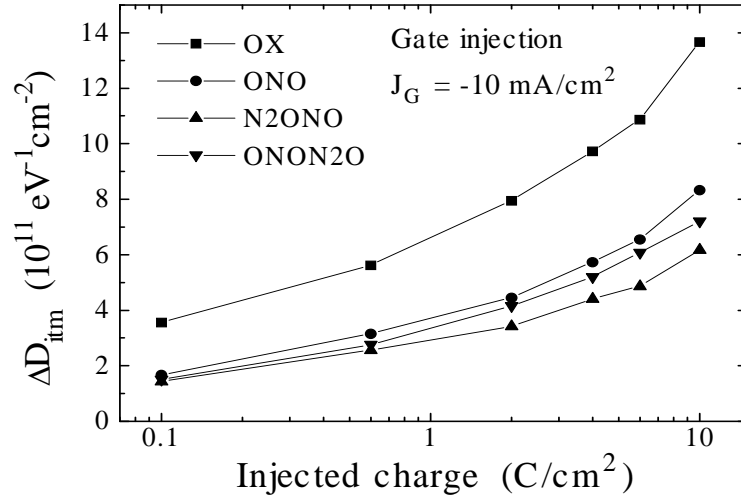
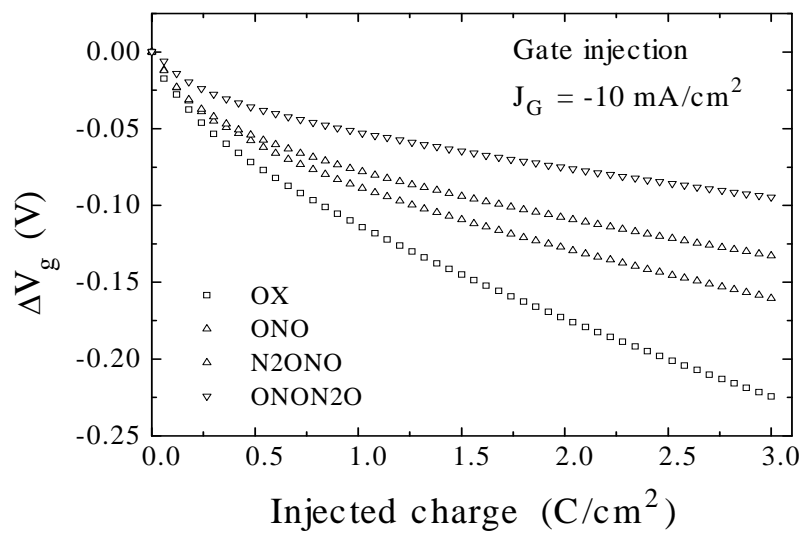
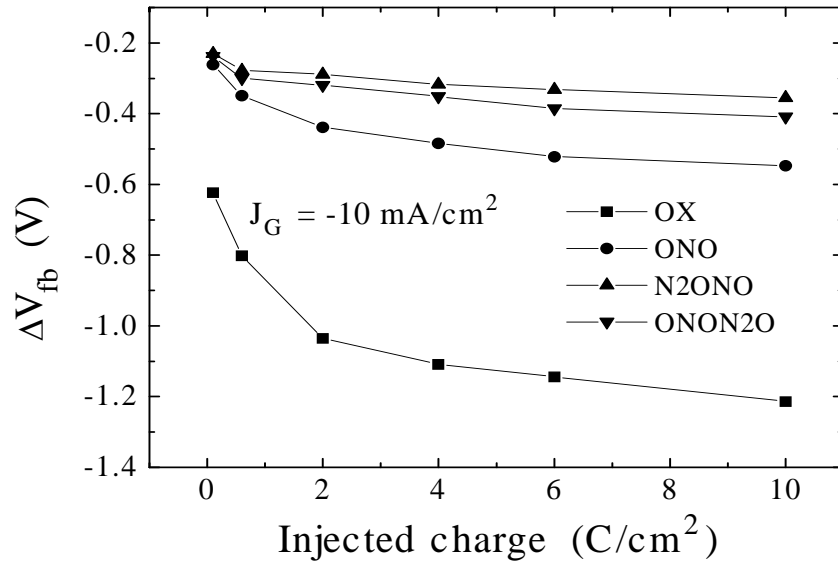


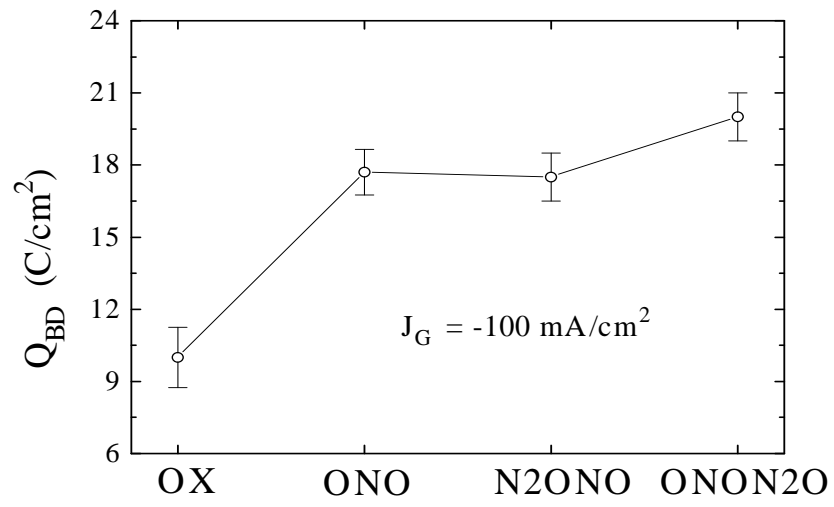
Fig. 2



**Fig. 3**



**Fig. 4**



**Fig. 5**