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Highly Reliable Thin Nitrided SiO_2 Films Formed by Rapid Thermal Processing in an N_2O Ambient

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Nitridation of thin SiO_2 film has been succeeded by rapid thermal processing (RTP) using only O_2 and N_2O as reactants. In comparison with pure SiO_2 film, nitrided SiO_2 (SiO_xN_y) film (8 nm), which includes about 5 at% nitrogen at the SiO_xN_y/Si interface, showed a large charge-to-breakdown value greater than 30 C/cm^2 and a density of electron traps lower than that of SiO_2 in high-field stressing (>8 MV/cm) under the condition of gate negatively biased. The SiO_xN_y/Si interface evaluated by high-resolution TEM is quite uniform, at least ordered within one or two atomic layers.

1. INTRODUCTION

Very thin SiO_2 films are strongly needed for advanced integrated circuits such as scaled EPROMs, EEPROMs and MOSFETs. In these MOS devices, dielectric films should have excellent leakage characteristics and high dielectric strength. The trapping characteristics are also important for keeping device reliability. The wear-out and hot-carrier injection of SiO_2 film due to high-field stress become to be more actualized with a decrease in the SiO_2 film thickness. To improve the dielectric properties, thermal nitridation of SiO_2 has been proposed[1-3]. Many activities in this field have been focused on the nitridation of SiO_2 with NH_3. Although NH_3-nitrided SiO_2 film has several advantages such as reduction of the interface trap states and blocking of impurity penetration, the inclusion of hydrogen atoms (H), which act as an origin of electron traps, is unavoidable. Reoxidation of this film has been proved to be effective in reducing included H atoms[4-6]. This process is, however, rather complicated and strongly dependent on its conditions.

To avoid the above complexity, we have successfully applied rapid thermal processing (RTP) to the nitridation of thin SiO_2 films. This process consists of the combination of in situ oxidation with O_2 and in situ nitridation with nitrous oxide (N_2O). In this paper, the dielectric properties of N_2O-nitrided SiO_2 (SiO_xN_y) film and the SiO_xN_y/Si interface structure will be described in comparison with pure SiO_2 film.

2. EXPERIMENTAL

SiO_2 and SiO_xN_y films were formed on 3-5 ohm cm, p-type (100) Si wafers after the standard cleaning procedure reported elsewhere[7,8] by the above oxidation and nitridation (or oxynitridation), in which the heating and cooling rates were 50-100°C/s. Table I shows the process sequences employed. For all samples #1, #2, #3 and #4, the total film thicknesses were 8.2 nm ± 0.5 nm. MOS capacitors were fabricated by depositing n^+ polysilicon gate electrodes on the dielectric films. MOS characteristics were evaluated by C-V, I-V and time-dependent dielectric breakdown (TDDB) measurements. The SiO_xN_y/Si

Table I. Preperation sequences employed in this study.

No.	RTON-1	RTO	RTON-2
#1	------	O_2,1100°C	------
#2	N_2O,1100°C	O_2,1100°C	------
#3	N_2O,1100°C	O_2,1100°C	N_2O,1100°C
#4	------	O_2,1100°C	N_2O,1100°C

interface was evaluated by high resolution TEM (HRTEM), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

3. RESULTS

3.1 Dielectric properties of SiO_xN_y films

To investigate the effect of stress on the MOS capacitors, electrons were injected, in the Fowler-Nordheim (F-N) region, from the gate electrode into the dielectric films at a constant current (-10 mA/cm^2). All measurements were performed on MOS capacitors with the gate area of $2x10^{-4}cm^2$.

The effect of the stress on the density of inteface trap states (D_{it}) as a function of injected charge (Q_{inj}) is shown in Fig.1. Sample #1 (pure SiO_2) showed a large increase in D_{it} at the initial stage. On the contrary, samples #2, #3 and #4 (SiO_xN_y) provide smaller ΔD_{it} values as compared to sample #1. Figure 2 shows the effect of the stress on the flatband voltage shifts (ΔV_{FB}). Although negative shifts of V_{FB} are found for all samples, the shifts of samples #2, #3 and #4 are much smaller than that of sample #1. The amount of ΔV_{FB} corresponds to the density of hole traps. Hence, the saturation tendency of V_{FB} in higher charge region exhibits hole trap filling process.

The gate voltage shifts (ΔV_g) at a constant current density are plotted in Fig.3. For sample #1, V_g is slightly shifted to the positive direction at the initial stage, and then increases almost linearly to the negative direction with increasing Q_{inj}. This nonsaturating increase of V_g is

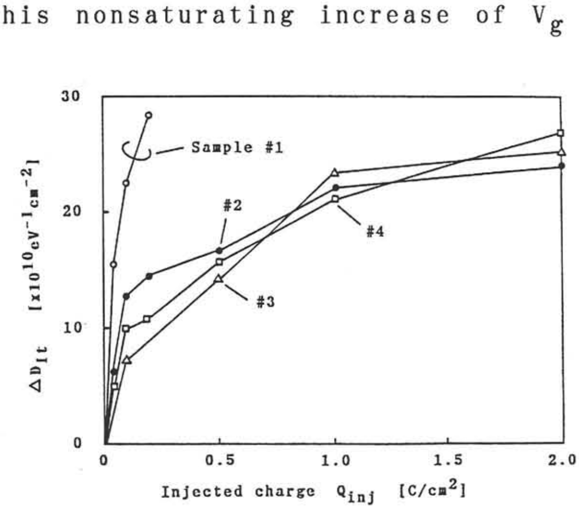

Fig.1 Interface trap density change as a function of the injected charge for samples #1-#4.

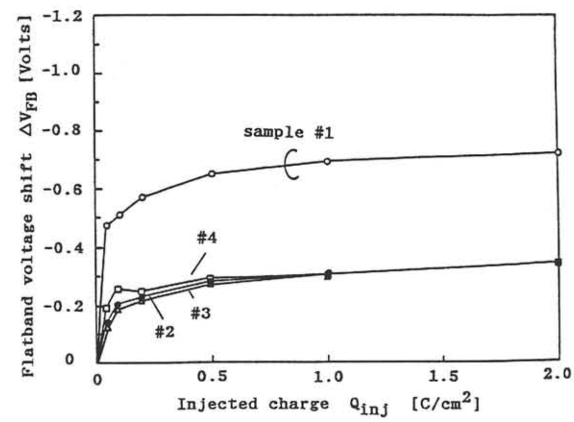

Fig.2 Flatband voltage shift as a function of the injected charge for samples #1-#4.

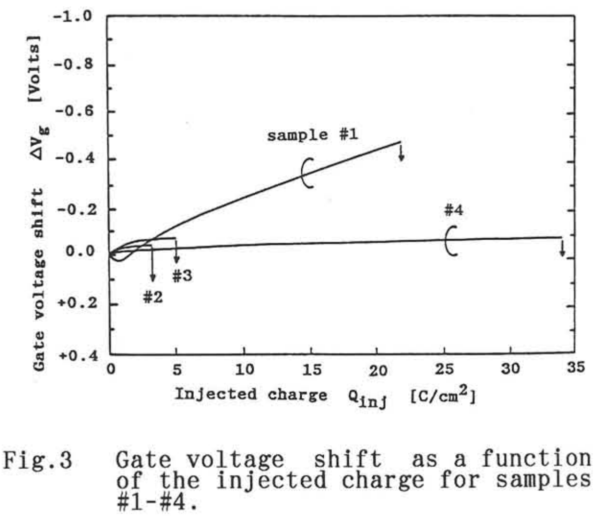

Fig.3 Gate voltage shift as a function of the injected charge for samples #1-#4.

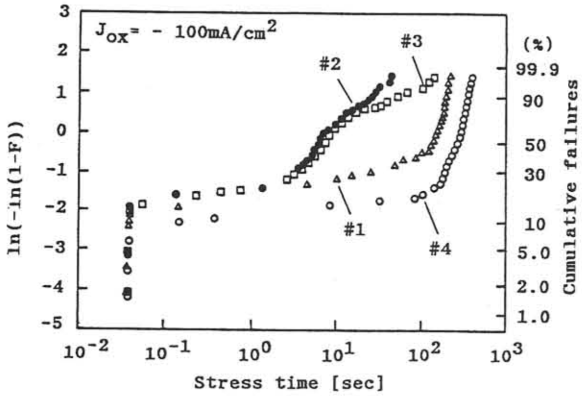

Fig.4 Cumulative failure-stress time relationships in the TDDB test of samples #1-#4.

attributed to the creation of new electron traps. On the contrary, for samples #2, #3 and #4, no positive V_g shifts are observed and the degrees of negative V_g shifts are much smaller than that in sample #1. As is seen in Fig.3, charge-to-breakdown (Q_{BD}) increased in the order : sample #2, #3, #1 and #4.

Figure 4 shows cumulative TDDB failures for all samples. It is apparent that sample #4 is superior to sample #1, but samples #2 and #3 are much inferior to sample #1. This finding indicates that proper nitridation (sample #4) is effective for improving the breakdown characteristics.

3.2 The SiO_xN_y/Si interface structure

The layer compositions of the oxide films were investigated by AES. The depth profiles of N, O and Si for sample #1 are shown in Fig.5. Nitrogen is not observed in the bulk or at the SiO_2/Si interface within detection limits. On the contrary, an accumulation of N of about 5 at% was observed at the interface of sample #4, as shown in Fig.6. Similar results were obtained for samples #2 and #3.

The chemical bonding state of N atoms at the SiO_xN_y/Si interface was investigated by XPS. Typical O(1s) and N(1s) core level spectra measured near the interface of sample #4 is shown in Fig.7. The N(1s) peak due to Si-N bonds is found at 397.8 eV. The O(1s) spectrum, whose main peak appears at 532.2 eV, indicates that the SiO_xN_y structure is essentially the same as tetrahedral SiO_4 itself.

The morphology of the SiO_xN_y/Si interface was evaluated by HRTEM. As shown

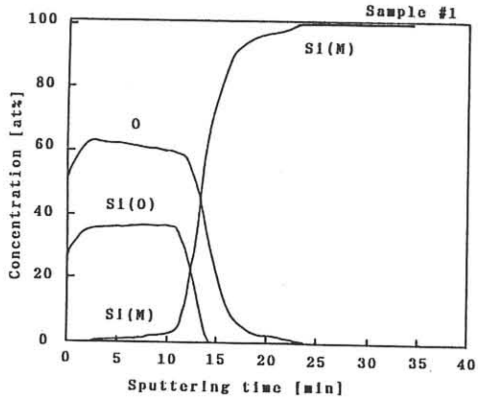

Fig.5 Auger depth profile of sample #1.

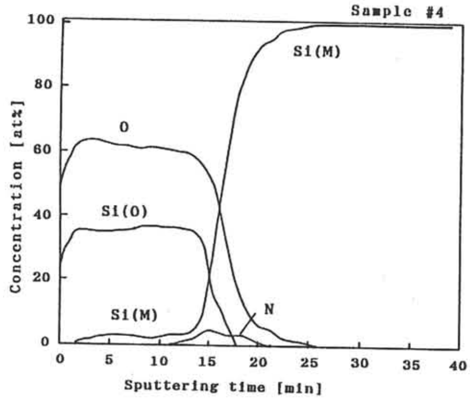

Fig.6 Auger depth profile of sample #4.

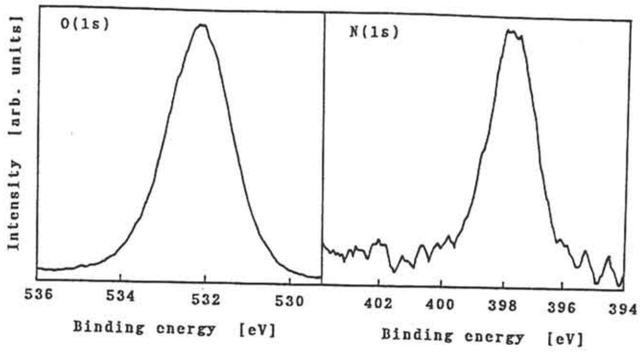

Fig.7 O(1s) and N(1s) core level lines in XPS spectra for sample #4.

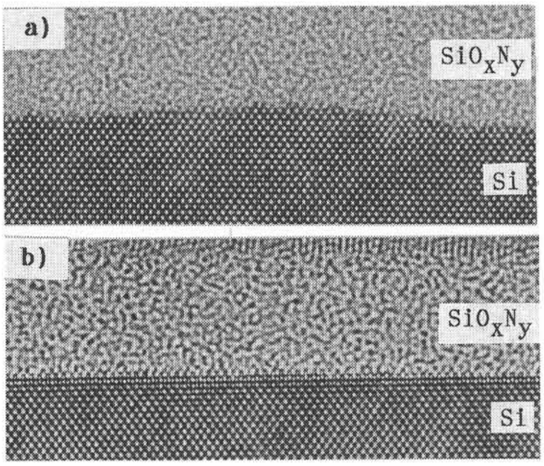

Fig.8 Cross sectional HRTEM images at the SiO_xN_y/Si interfaces of samples #3 (a) and #4 (b).

in Fig.8, HRTEM images show that the SiO_xN_y/Si interface in sample #4 is quite uniform at least ordered within one or two atomic layers, whereas unduration up to 1 nm and thickness inhomogineity are observed in samples #2 and #3.

4. DISCUSSION

The SiO_xN_y film formed by RTP indicates smaller changes in the densities of electron and hole traps and in D_{it} as compared with SiO_2 film.

These differences between the pure SiO_2 and SiO_xN_y film can be explained on the basis of the broken bond model[9-11]. In SiO_2 film, defects such as strained Si-O, Si-O-O-Si and/or Si-OH groups are present. This model indicates that when the above defects are scissored off by injected electrons, a large number of trivalent silicon, Si^* ($O_3\equiv Si^\bullet$ and/or $Si_3\equiv Si^\bullet$), which act as hole traps, is generated and that they induce positive charge by processes such as $O_3\equiv Si^\bullet + h \rightarrow O_3\equiv Si^+$. Injected electrons are captured simultaneously by the process : $O_3\equiv Si^+ + e^- \rightarrow O_3\equiv Si^\bullet$. If the above Si^* defects are minimized by the formation of Si-N bonds near the SiO_xN_y/Si interface, the hole trappng rate can be reduced, resulting in decreases ΔD_{it} and in positive charge density. The formation of Si-N bonds plays also an important role in reducing electron traps.

In the V_g measurements, only sample #4 showed a large Q_{BD} value greater than 30 C/cm^2 as compared to that of sample #1. On the contrary, Q_{BD} values for samples #2 and #3 are much smaller than that of sample #1. The detailed mechanism of breakdown phenomena is still unknown. However, for samples #2 and #3, film thickness inhomogineity and large undulation at the interface have been confirmed by HRTEM. Hence, we consider that localization of electric field and charge build up occur in samples #2 and #3, resulting in smaller Q_{BD} values. On the other hand, sample #4 has atomically flat interface as is similar to thin SiO_2 film previously reported[7,8], consistent with its excellent dielectric properties.

5. CONCLUSION

A new and reliable method of nitridation of thin SiO_2 film has been developed by employing the following RTP sequence : oxidation in O_2 and nitridation (or oxynitridation) in N_2O. The dielectric properties of SiO_2 film can be greatly improved by this process.

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