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Improvement of Breakdown Characteristics of the Gate Oxynitride Using N_2O

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Abstract: Charge trapping and dielectric breakdown (Q_{bd}) properties of rapidly thermal gate oxynitrided (RTON) films have been studied using N_2O. The gate voltage shift (ΔV_G) has been used to characterize the charge trapping properties under Fowler-Nordheim electron injection from Si substrate. It is found that RTON with N_2O can reduce ΔV_G resulting from the reduction of trapped electrons. Oxynitridation characteristics in N_2O is also discussed. Oxynitridation characteristics can not be explained as classical Deal-Grove model. Deal-Drove model is modified to fit theoretical curve to experimental data.

Keywords: N_2O Oxynitridation, RTO, Modified Deal-Grove Model, TDDB, Charge trapping

1. Introduction

Recently, flash memory has been realized as a high density nonvolatile memory. In the performance of flash memory, high electric field (>10MV/cm) is applied to the gate oxide and Fowler-Nordheim (FN) tunneling current flows in the ultra thin gate oxide. These high electric field or electron injection into the gate oxide degrades the gate dielectric characteristics such as increase of tunneling current at lower electric field (3~5MV/cm) or threshold voltage shift by the charge trapped in the oxide[1)2)]. More reliable gate insulator to withstand high electrical stress is needed than conventional thermal oxide.

Nitridation of gate oxide is known to play an efficient roll to improve oxide characteristics for electrical stress. In the nitridation of gate oxide, strong Si-N bond is formed instead of strained weak Si-O bond in the oxide structure and bond-breakup by the collision of electron injected into the oxide is reduced[3)4)].

Various nitridation processes have been investigated in NH_3 or N_2O gas ambient [5)6)]. In this work, we investigate the degree of improvement of electrical characteristics under high field stressing of the films oxynitrided in pure N_2O by comparing to conventional dry and wet O_2 oxidation. As same as good breakdown characteristics for electrical stress, low interface trap density is needed for high quality gate oxide. Interface state density evaluated by Quasi Static C-V measurement is also discussed in this report.

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2. Experimental

MOS capacitor is fabricated on n-type (100) CZ Si substrate (3~5 Ω · cm). Si substrate is cleaned with SC1(NH_4OH: H_2O_2: H_2O = 1:5:20) RCA cleaner for 10min at 60℃, then rinsed in deionized water for 15min. Gate oxidation is carried with RTO (Rapid Thermal Oxidation) in dry O_2, wet O_2 and pure N_2O atmosphere. Additional annealing is not carried in this experiment. Wet O_2 gas are generated by bubbling dry O_2 in ultra pure water at room temperature. **Fig.1** shows the apparatus of RTO in this experiment. Substrate temperature is monitored by pyrometer and controlled by computer system for the range from 450 ℃ to 1350 ℃. Substrate temperature is cooled down to room temperature with 5 ℃/sec after RTO in this experiment. Oxidation temperature and heating rate are controlled to be 1050 ℃ or 1150℃ and 125 ℃/sec in this experiment.

Gate oxide thickness are measured by single wavelength ellipsometry (He-Ne 632nm). It is known that accuracy of the refractive index is degraded for thin film measurement by ellipsometry[7)]. Therefore refractive index oxidized in dry O_2 and wet

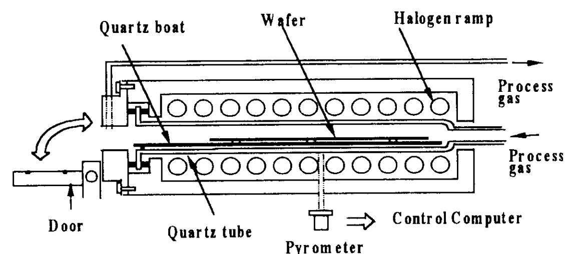

Fig.1 The apparatus of RTO in this experiment.

O_2 is fixed to be theoretical value of SiO_2 (1.46) in this experiment. However, refractive index of the oxynitride film is changed with the percentage of the N atom in the oxide. In this experiment, refractive index oxidized in pure N_2O for 130sec (most thicker film for N_2O oxidation in this experiment) is evaluated to be 1.56 for both oxidation temperature by 2 incident angle ellipsometry measurement with the assuming 2 layer model ($SiO_2/SiO_xN_y/Si$). It was reported that refractive index of the oxynitride films fabricated with almost same condition is 1.5-1.6 which is as same as measured value in this experiment[3]. Thus refractive index of the oxynitride film is fixed to be 1.56 for the oxidation time less than 130sec in this experiment.

Al is evaporated in vacuum chamber with resistance heating on gate oxide as metal contact for the measurement of TDDB (Time Dependent Dielectric Breakdown) and gate voltage shift to maintain constant current injection into the oxide. Evaporated Al is patterned by photo lithography and wet etching in phosphorus acid (65℃). The electrode area of patterned Al is $0.001225cm^2$. Constant Fowler-Nordheim tunneling electrons are injected from Si substrate at the current density of $10mA/cm^2$ for the measurement of TDDB and gate voltage shift (ΔV_G). ΔV_G is proportional to the charge density trapped in the oxide by electron injection. Interface state density is evaluated with Quasi-Static C-V (Q C-V) measurement with HP4140B. Ramp voltage of 0.01V/sec is applied to gate electrode for Q C-V measurement.

3. Results

3.1 Oxidation characteristics

Fig.2 shows oxidation characteristics in dry O_2 and pure N_2O as a parameter of oxidation temperature. Just before RTO, Si substrate was subjected into BHF to remove native oxide for the measurement of oxidation characteristics. Therefore initial thickness of the oxide is considered to be 0Å.

Several features can be observed in this figure. First, the oxidation rates in pure N_2O are much slower than the rate in dry O_2 for both oxidation temperature. Second, oxide growth rates in N_2O saturates significantly after the film thickness reach about 40Å for both oxidation temperature.

The classical Deal-Grove model was not applicable for this rapid growth in early stage. Several models were proposed to explain these rapid growth in pure N_2O oxidation[8)9)10)]. They proposed the formation of a nitrogen rich interfacial layer as dif-

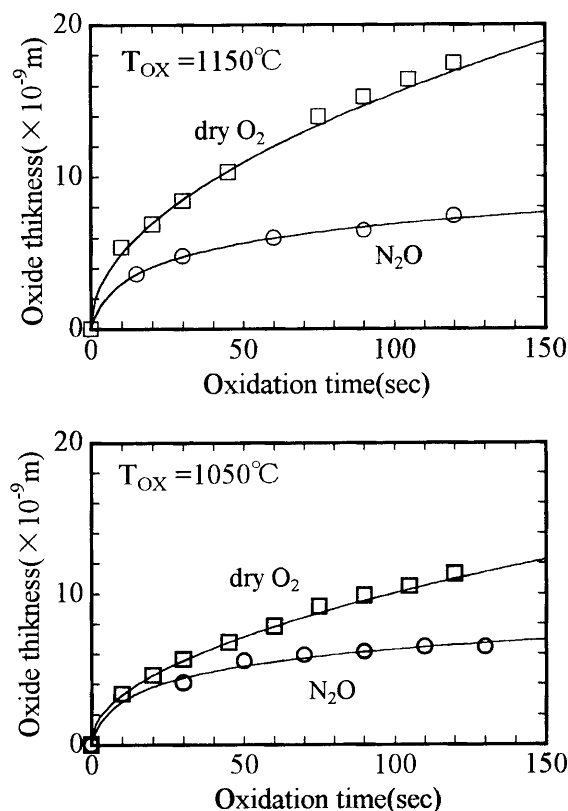

Fig.2 Oxidation characteristics in dry O_2 and N_2O as a parameter of oxidation temperature.

fusion barrier for the oxidant or the neutralization of oxidation reaction site by the nitrogen atom. Mechanism of oxidation in pure N_2O is discussed in latter section in this report.

3.2 Interface state densities

Fig.3 shows the distributions of interface state density as a parameter of oxidation gas. In dry O_2 oxidation, anomalous hump of interface state density is appeared in upper half in band gap (at 0.75eV). These anomalous hump in upper half in band gap is observed in the oxide exposed to VUV (Vacuum Ultra Violet) radiation or injected hot electron. Previous results suggests that these anomalous hump is associated to trap to trap tunneling from interface state to near interface oxide trap at low frequency[11)]. This anomalous hump can be disappeared by RTO in wet O_2 or N_2O. Moreover interface state density at mid gap can be reduced by oxidation in wet O_2 or N_2O as compared with dry O_2. It is well known that interface state is an unpaired electron which is not bonded to O atom (dangling bond) at interface[12)]. Therefore hydrogen or nitrogen atom are able to act as termina-

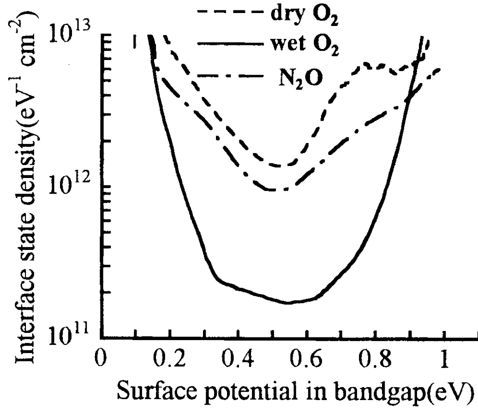

Fig.3 Influence of oxidation gas on the characteristic of interface state density. In dry RTO, anomalous hump of interface state density is appeared in upper half in band gap. This anomalous hump is disappeared in wet O_2 and N_2O oxidation.

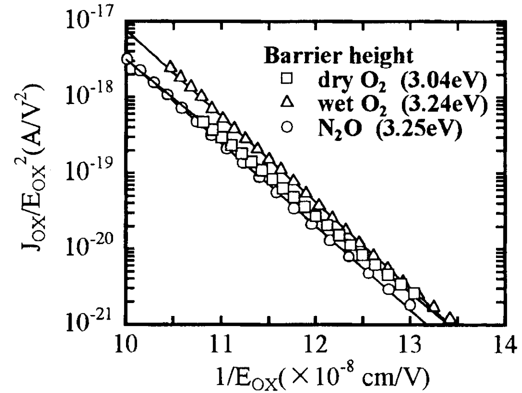

Fig.4 Fowler Nordheim tunneling plots for the oxides fabricated in dry O_2, wet O_2 and N_2O atmosphere. Barrier heights for wet O_2 and N_2O oxidation are higher than dry O_2. This means that structural defect at SiO_2/Si interface is smaller for wet O_2 and N_2O oxidation.

tion species for the dangling bond by the formation of Si-H or Si-N bond. Moreover, it is also reported that atomic scale flat SiO_2/Si interface is formed in wet O_2 or pure N_2O oxidation by the stress relaxation at interface with the formation of Si-H or Si-N bond structure[13)14)]. This leads to the reduction of interface state density oxidized in wet O_2 or pure N_2O. Interface state density is much more reduced in wet O_2 oxidation than in N_2O oxidation. Hydrogen atom is more effective to reduce interface state density than N atom.

3.3 Fowler-Nordheim plots

Fig.4 shows the plots of Fowler-Nordheim (FN) tunneling current in the oxide fabricated in dryO_2, wetO_2 and pure N_2O. Tunneling electron is injected from Si substrate. It was reported in some studies that tunneling current in oxynitride films oxidized in pure N_2O can not be described as Fowler-Nordheim tunneling mechanism[15)]. However, our experimental result shows tunneling current of the oxynitride film fabricated in pure N_2O can be described as Fowler-Nordheim tunneling as shown in **Fig.4**. Barrier heights at SiO_2/Si interface calculated from FN plots are also shown in **Fig.4**. Barrier heights fabricated in N_2O and wet O_2 show higher values (~3.25eV) than dry O_2 oxidation (3.04eV). This means that much more structural defects exists at SiO_2/Si interface oxidized in dry O_2 than in N_2O or wet O_2.

3.4 Improvement of the immunity for electrical stressing by N_2O oxidation.

Fig.5 shows the gate voltage shift to maintain constant current injection into the oxide. Hot electron is injected using Fowler-Nordheim tunneling from Si substrate. Gate voltage shift is associated to trapped charge density in the oxide as follows equation.

$$\Delta V_G = -N_{ox}q/C_o \quad (1)$$

Where, N_{ox} is centoroide weighted charge density in the oxide. C_o is a capacitance of the oxide. FN electron is injected from Si substrate at $10mA/cm^2$. Since electron is injected from Si substrate, charge build up near the SiO_2/Si interface should have a greater moment in ΔV_G. Positive gate voltage shift means that electron is trapped in the oxide and negative shift means hole trapping. As shown in **Fig.5**, hole is trapped early stage in electron injection and then electron is trapped in the oxide. This is corresponded to larger trap cross section of hole as compared with electron.

Trapped charge density in the oxide fabricated in N_2O is smallest than the samples oxidized in dry O_2 or wet O_2. In N_2O oxidation, strained weak Si-O bond near interface is removed by forming strong Si-N bond. Strained Si-O bond can be easily broken up by the non elastic collision to hot electron and injected electron is trapped by dangling bond. Thus bond-breakup near interface by hot electron impact is smaller for the oxide fabricated in N_2O than in wet O_2 or dry O_2 oxidation. In wet oxidation, many Si-H bond is formed in the oxide and

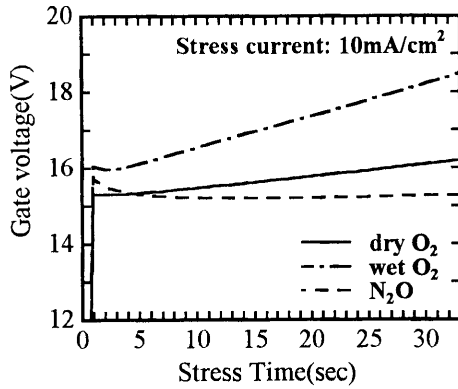

Fig.5 Gate voltage shift to maintain constant current injection into the oxides. Oxide thickness of dry O_2, wet O_2 and N_2O are 167, 165 and 157Å respectively. Oxidation in N_2O shows smallest charge trap density for current injection.

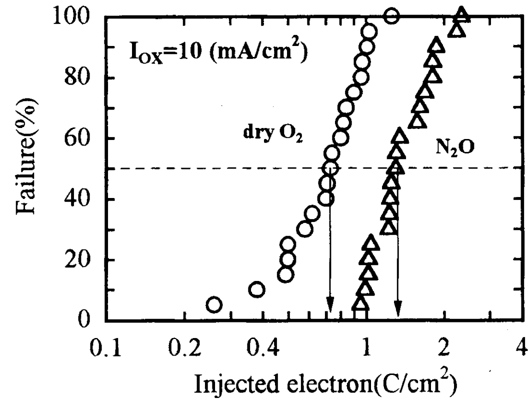

Fig.6 TDDB characteristics of the oxides fabricated in dry O_2 and pure N_2O. Oxides thicknesses are 167 and 157Å for dry O_2 and pure N_2O.

atomic scale flat SiO_2/Si interface is formed by deoxidization of strained week Si-O bond by hydrogen atom. This leads to the result of less interface trap density as shown in **Fig.3**. However, Si-H bond energy is smaller (3.2eV) as compared with Si-N bond and Si-H bond is easily depassivated by hot electron injection. Therefore largest ΔV_G shift is observed in the wet oxide.

Fig.6 shows TDDB characteristics of the films fabricated in dry O_2 and N_2O. Constant electron current is injected into the oxide and time to break down is measured. Stress current is injected from Si substrate at $10mA/cm^2$ for both samples. Oxide thickness are 167, 165 and 157Å for dry O_2, wet O_2 and N_2O respectively. Charge to 50% cumulative failure (Q_{bd}) are $0.7C/cm^2$ and $1.5C/cm^2$ for dry O_2 and N_2O respectively. This improvement in Q_{bd} may be related to the reduction of charge trapping for oxidation in N_2O.

4. Discussion

It was reported that classical Deal-Grove model can not explain the experimental data in the region of initial rapid growth in pure N_2O oxidation. Many modification of classical Deal-Grove models are proposed. Ditrijev *et al.* proposed the reduction of oxidation reaction site by the effect of N atom neutralization at interface[10]. W. Ting *et al.* proposed the decrease of diffusion coefficient of the oxidant in the oxide by the formation of N-rich layer as diffusion barrier. In this report, we modify the classical Deal-Grove model by the assumption of non steady state distribution of the oxidant in the oxide.

In the classical Deal-Grove model, oxidation characteristics can be explained by flux continuous condition of the oxidant. **Fig.7** shows schematic diagram of the distribution of oxidant in the oxide. Flux of the oxidant in the oxide and at SiO_2/Si interface is described as follows.

$$F_{ox} = D\frac{C_s - C_{it}}{x} \tag{2}$$

$$F_{it} = kC_{it} = C_{ox}\frac{dx}{dt} \tag{3}$$

Here, F_{ox} and F_{it} are the oxidant flux in the oxide and at the interface of SiO_2/Si. C_s and C_{it} are the oxidant density at oxide surface and at interface. D is the diffusion coefficient of the oxidant in the oxide. k is the reaction coefficient of oxidation reaction at interface. x is the oxide thickness. C_{ox} is the number of the oxidant which is incorporated into the unit volume of oxide.

With the condition of $F_{ox} = F_{it}$,

$$C_{ox}\frac{dx}{dt} = kC_s\frac{1}{1 + kx/D} \tag{4}$$

If oxide thickness is small (x <200Å) then oxidation characteristics becomes linear characteristics and described as follows.

$$\frac{dx}{dt} = k\frac{C_s}{C_{ox}} \tag{5}$$

Equation (2) is obtained by the Fick's low with the assuming of linear distribution of the oxidant which is consistent if oxidation is in steady state. However, in pure N_2O oxidation, D or k is changed dependent on the oxidation time with the formation

of N-rich layer or the neutralization of oxidation reaction cite by N atom. Therefore, oxidation in pure N_2O is not steady state and distribution of the oxidant is not linear distribution. Equation(2) at the interface region must be changed as follows.

$$F_{ox} = -D\frac{dC_{it}}{dx} \tag{6}$$

From $F_{ox} = F_{it}$,

$$-D\frac{dC_{it}}{dx} = kC_{it} \tag{7}$$

This equation can be solved with $C_{it} = C_s$ at t = 0.

$$C_{it} = C_s exp(-\frac{k}{D}x) \tag{8}$$

From this equation, the oxidant at interface is decreased with increasing oxide thickness. With the equation (3) and equation (8),

$$\frac{dx}{dt} = k\frac{C_s}{C_{ox}}exp(-\frac{k}{D}x) \tag{9}$$

This differential equation can be solved with the condition of $x = x_o$ at t = 0,

$$x = \frac{D}{k}\ln[exp(kx_o/D) + \frac{C_s k^2 t}{C_{ox}D}] \tag{10}$$

As shown in equation(10), oxide thickness is rapidly increased in early stage of oxidation. However with increasing oxidation time, oxidation rate is saturated.

Fitting results by least square method to the experimental data is shown in **Fig.2**. Good agreement to measured data is achieved using equation(10). On the other hand, oxidation characteristics in dry O_2 can be fitted with classical Deal-Grove model as shown in **Fig.2**.

Oxidation characteristics in dry O_2 shows parabolic characteristics even in thin oxide thickness region. It is known that strong compressive stress is generated at the SiO_2/Si interface during dry O_2 oxidation due to no relaxation species for strained Si-O bond such as hydrogen in the oxide[16]. These strong compressive stress in the oxide caused decrease of diffusion coefficient and oxidation characteristics may be parabolic even in the region of thin oxide thickness.

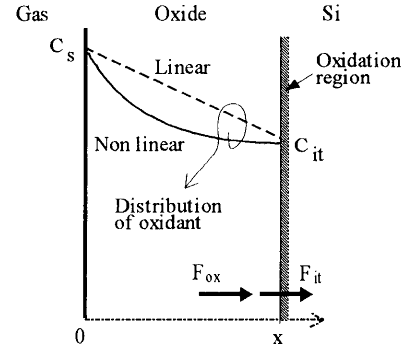

Fig.7 Schematic diagram showing the oxidant density in the oxide. Classical Deal-Grove model is assumed linear distribution of the oxidant in the oxide as shown in dashed line.

5. Summary

We summarize the results on the characteristics of the oxide fabricated in pure N_2O in this experiment as follows.

(1) Rapid increase of oxide thickness is observed in pure N_2O oxidation at early stage . These rapid increase can be well fitted by the modified Deal-Grove model with the assumption of non linear distribution of oxidant in the oxide.

(2) Interface state density can be reduced by oxidation in N_2O as compared with dry O_2. However, Oxidation in wet O_2 shows lowest interface trap density than the other oxidation gas in this experiment. Hydrogen or nitrogen atom can effective to terminate the dangling bond at SiO_2/Si interface.

(3) All tunneling current in the oxides fabricated in dry O_2, wet O_2 and N_2O can be explained as Fowler-Nordheim tunneling mechanism. Barrier height at SiO_2/Si interface for wet O_2 and N_2O oxidation show higher value than dry O_2 oxidation. This indicates lower interface structural defect is exit in wet O_2 or N_2O oxidation.

(4) Oxidation in N_2O leads to increase the time to breakdown of the oxide as compared with dry O_2 oxidation. From the results of ΔV_G, less electron traps are generated in the oxide fabricated in pure N_2O than dry O_2 oxidation. This may be caused that oxide film fabricated in N_2O has strong bond structure (Si-N) to hot electron impact instead of strained weak Si-O

bond existed in the oxide fabricated in dry O_2. ΔV_G for wet O_2 oxidation shows largest value. This means that Si-H bond is more easily broken by hot electron impact than Si-N bond. It is need to reduce hydrogen atom in the oxide for high reliability for high field stressing.

From the result of TDDB characteristics and gate voltage shift by hot electron injection, Electrical characteristics of the oxide under high field stressing can be improved by N_2O oxidation. Direct rapid thermal oxynitridation in pure N_2O is effective to fabricate high reliable gate oxide for high field stressing.

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