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# Optimization of Nitridation and Re-oxidation Conditions for an EEPROM Tunneling Dielectric

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We show that the re-oxidation time is a very useful global parameter to determine an optimum re-oxidized nitrided oxide (RONO) film processing condition. Using such an optimized condition, we formed a RONO film as an EEPROM tunnel dielectric. The film is found to not only drastically improve the endurance characteristics of but also cause no degradation at all to the characteristics of the 1M bit EEPROM devices actually fabricated.

## 1. Introduction

It has recently reported that re-oxidized nitrided oxide (RONO) films fabricated by rapid thermal processing are preferable to pure $SiO_2$ in many aspects, when they are used as thin gate dielectrics of MOSFETs and tunneling dielectrics of EEPROMs(1). However, many processing parameters are involved in the fabrication of an RONO film, such as nitridation time, temperature, ambient, re-oxidation time and temperature, it is difficult to optimize all of them.

In this paper, we show that the re-oxidation time is a very useful parameter to represent the characteristics of RONO films globally. Using this parameter, we fabricated a RONO film that has no window narrowing. We used this optimized RONO film as a tunneling dielectric for 1M bit EEPROMs. We found that the film not only drastically improve the endurance characteristics of but also cause no degradation at all to the EEPROM devices.

## 2. Characteristics of RONO Films

Figure 1 shows the results of a constant current stressing test of rapid thermal nitrided oxide (without re-oxidation). The 8 nm thick oxide film to be nitrided is thermally grown by wet oxidation in a conventional furnace. The capacitor area is 0.1 $mm^2$ and the stress current density is 1.0 $A/cm^2$. The vertical axis represents the amount of injected charge to breakdown and the horizontal axis indicates the nitridation condition numbers where for each such number the nitridation process condition is listed in Table 1. The conditions are arranged in increasing order of the amount of

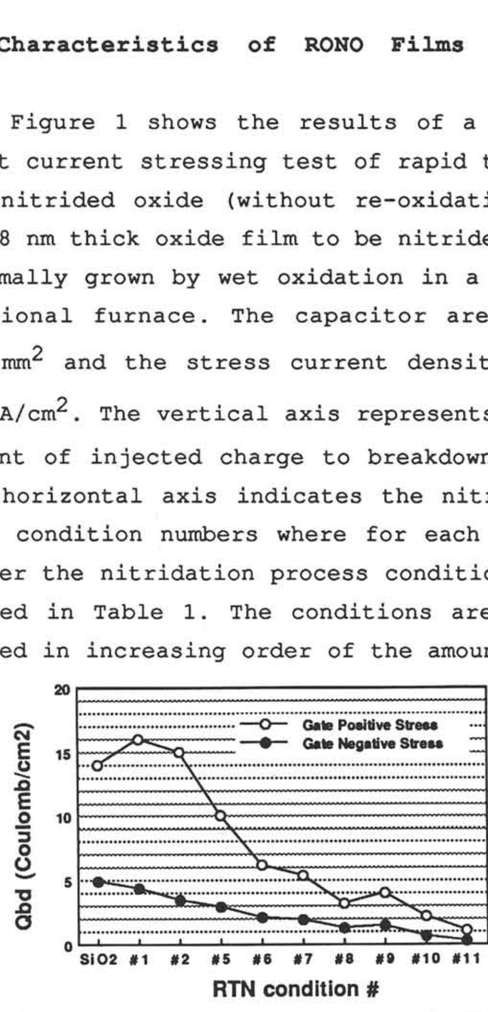


**Fig.1.** Constant current stress TDDB measurement of rapid thermal nitrided oxides. Nitridation condition dependence of $Q_{bd}$.

| RTN Condition # | Nitridation Condition |
|---|---|
| #1 | 950C 10% NH3 30sec |
| #2 | 950C 20% NH3 30sec |
| #5 | 900C 100% NH3 30sec |
| #6 | 950C 100% NH3 30sec |
| #7 | 1000C 50% NH3 30sec |
| #8 | 1150C 50% NH3 30sec |
| #9 | 1000C 100% NH3 30sec |
| #10 | 1050C 100% NH3 30sec |
| #11 | 1100C 100% NH3 30sec |

**Table 1.** Rapid thermal nitridation conditions.

the nitridation. That is, the larger the condition number, the heavier the nitridation condition. Note that each nitridation condition number of Table 1 coincides with a RONO condition number shown in Table 2. The ordering method of these conditions is explained later. Figure 1 clearly indicates that when no re-oxidation is done the reliability of dielectrics drastically decreases as the degree of nitridation increases.

On the other hand, Figure 2-a shows the results of a constant current stressing test for the re-oxidation condition dependence of a nitrided oxide. The nitridation condition is fixed at the temperature of 1100 C and annealed for 30 secs in 100% $NH_3$ ambient. The re-oxidation temperature is 1100 C and the re-oxidation time is varied from 10 secs to 300 secs. The horizontal axis in Figure 2-a represents the re-oxidation time. Since re-oxidation of 300 secs shows a 10% increase in thickness (about 9 nm thick after re-oxidation), it is considered to be the maximum re-oxidation condition at this nitridation condition. The results obtained in Figure 2-a show that as the re-oxidation becomes heavier, its reliability on current stressing in gate positive stressing condition becomes higher as previously reported[1].

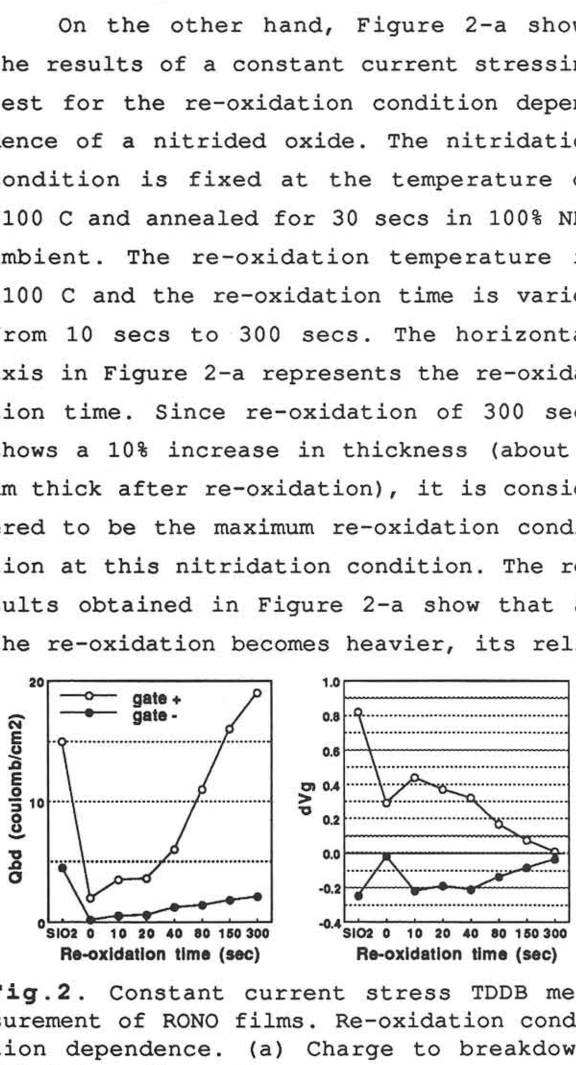


**Fig.2.** Constant current stress TDDB measurement of RONO films. Re-oxidation condition dependence. (a) Charge to breakdown. (b) Gate voltage change.

Figure 2-b shows the amount of differences between the the gate voltages taken at the start of the TDDB measurement and at a time immediately before the breakdown (dVg), to maintain a constant current. The dVg tends to be zero at heavier re-oxidation conditions, which is a very important factor for EEPROMs' tunnel dielectrics. This is because the endurance characteristics of EEPROMs is limited not by the breakdown of a tunnel dielectric but by the window narrowing caused by electron trapping in the tunnel dielectric. From the results mentioned above and those previously reported[1][2], it is expected that the heavier nitridation and the heavier re-oxidation of the tunnel dielectrics of EEPROMs are very effective to improve their endurance characteristics. However, it is difficult to determine an optimum RONO processing condition for a certain $SiO_2$ thickness within the limit of allowable heat treatment, since many process parameters must be optimized.

## 3. Optimization of RONO Conditions

As we will witness later, the maximum re-oxidation time is a good parameter to globally represent the amount of nitridation and the RONO film characteristics. In our experiments, the re-oxidation temperature is fixed at 1100 C. And the maximum re-oxidation time is defined to be the one for which the thickness of a nitrided oxide film gains a 10% increase.

| RONO condition # | Nitridation Condition | Re-oxidation Condition |
|---|---|---|
| #1 | 950C 10% NH3 30sec | 1100C O2 10sec |
| #2 | 950C 20% NH3 30sec | 1100C O2 20sec |
| #3 | 850C 100% NH3 30sec | 1100C O2 30sec |
| #4 | 950C 50% NH3 30sec | 1100C O2 50sec |
| #5 | 900C 100% NH3 30sec | 1100C O2 50sec |
| #6 | 950C 100% NH3 30sec | 1100C O2 60sec |
| #7 | 1000C 50% NH3 30sec | 1100C O2 80sec |
| #8 | 1050C 50% NH3 30sec | 1100C O2 120sec |
| #9 | 1000C 100% NH3 30sec | 1100C O2 200sec |
| #10 | 1050C 100% NH3 30sec | 1100C O2 260sec |
| #11 | 1100C 100% NH3 30sec | 1100C O2 300sec |

**Table 2** RONO processing conditions.

Table 2 shows the eleven RONO process parameters obtained by the criterion mentioned above. They are arranged in increase order of the re-oxidation time. Using this criterion, a very wide variety of RONO processing conditions in which the temperature varies from 850 C to 1100 C and the ammonia percentage ranges from 10% to 100%, can be represented globally by only one parameter. Figure 3-a shows the results of the constant current stress TDDB measurements of RONO films of the eleven types ($t_{eff}$=9 nm). The amount of charge to breakdown varies systematically with RONO conditions. This validates our claim that the re-oxidation time is a global parameter to represent nitridation conditions and film characteristics. Heavier nitridation yields more tolerance of charge injection, in the gate positive bias condition as reported in previous work[1]. On the other hand, in the gate negative bias condition, our results show that heavier nitridation causes less tolerance of charge injection. This implies that heavier nitridation and heavier re-oxidation do not always lead to higher reliability.

Figure 3-b shows the RONO condition dependence of the gate voltage change (dVg) during the constant current stress TDDB measurement. It should also be noted that dVg varies systematically with RONO conditions. Furthermore, in RONO conditions heavier than 8, no gate voltage change occurs in both the gate negative and positive stress conditions. Based upon the results mentioned above and the following three guidelines, RONO condition-8 is chosen to form a tunnel dielectric for 1M bit EEPROMs.

(1) Minimize the dVg, because the endurance characteristics of EEPROMs are limited not by the breakdown of the tunneling dielectric but by the window narrowing which is related to the amount of dVg.

(2) Minimize the nitridation to prevent the degradation of charge to breakdown characteristics in gate negative bias stress.

(3) Minimize the heat treatment of RONO processing to prevent the device characteristics degradation.

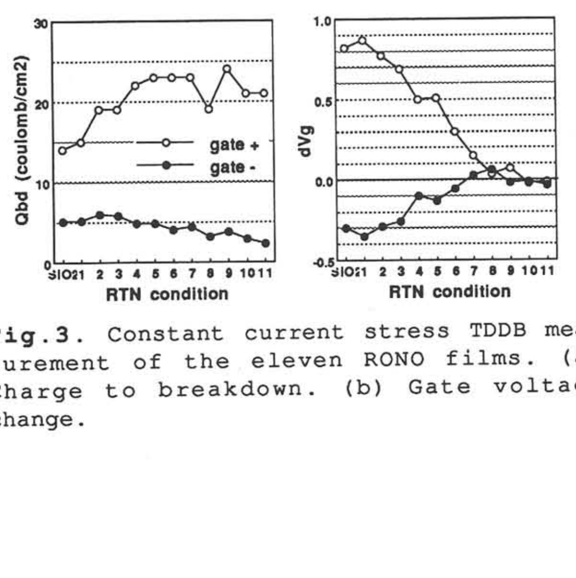

**Fig.3.** Constant current stress TDDB measurement of the eleven RONO films. (a) Charge to breakdown. (b) Gate voltage change.

## 4. Application to EEPROM Tunnel Dielectric

Figure 4 shows the cell structure of a 1M bit EEPROM using this RONO dielectric. The EEPROM was fabricated using an 1.0 µm lithography and triple level polysilicon process. The cell has a floating gate sandwiched between two control gates as in the case of the SSTR cell already presented by the authors[3]. In this cell structure, floating gate electrodes are formed by the second polysilicon and those for select gates and the gates of other MOS transistors are formed by the first polysilicon. The RONO process, except additional heat treatment, only affected to tunnel dielectrics but not gate oxides of other transistors.

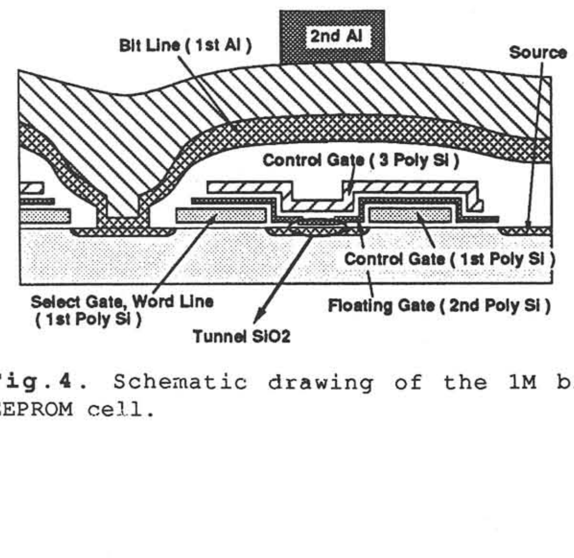

**Fig.4.** Schematic drawing of the 1M bit EEPROM cell.

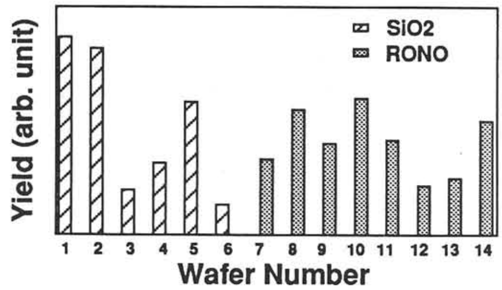


**Fig.5.** Yield of 1M bit EEPROM chips using pure $SiO_2$ and RONO tunnel dielectrics.

Figure 5 shows the yields of the 1M bit EEPROM with and without a RONO tunnel dielectric. Note that there is no disparity in the yield of the 1M bit EEPROM between the RONO tunnel dielectric devices and the pure $SiO_2$ tunnel dielectric devices. Figure 6 shows the EEPROM cell erase/write characteristics of RONO and pure $SiO_2$. It should also be noticed that there is no difference in the cell erase/write characteristics between the two tunnel dielectrics. It is not shown here but confirmed that there is no difference in other electrical characteristics such as transistor performance. The above results enable us to conclude that the heat treatment of RONO process condition-8 causes no degradation on the 1M bit EEPROM device characteristics and yield.

Figure 7 shows the endurance characteristics of a single bit cell. At $10^6$ cycle stressing, the pure SiO2 device shows a 20%-40% window narrowing while the RONO tunnel dielectric cell exhibits a window narrowing of less than 5%. Therefore RONO films are very useful to improve the endurance characteristics of the actual 1M bit EEPROM devices.

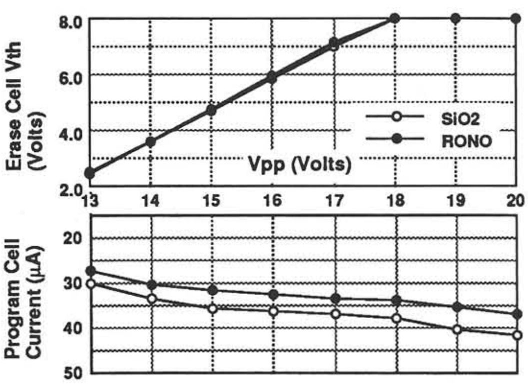


**Fig.6.** Cell erase/write characteristics of the 1M EEPROM using pure $SiO_2$ and RONO tunnel dielectrics.

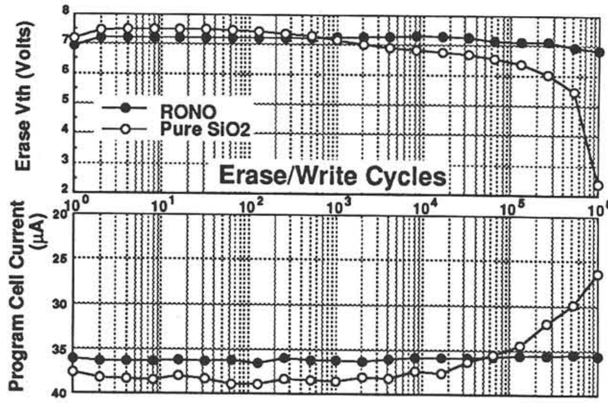


**Fig.7.** Endurance characteristics of the single bit cells of using pure $SiO_2$ and RONO tunnel dielectrics.

## 5. Conclusion

We find that the re-oxidation time is a global parameter to represent the characteristics of re-oxidized nitrided oxide films. Since many RONO process parameters have a close relationship to only one parameter, it is easy to find an optimum RONO condition. The optimized RONO film is used as a tunnel dielectric for a 1M bit EEPROM, and it is shown to be very useful to improve the endurance characteristics of the actual EEPROM devices without any degradation.

## 6. Acknowledgments

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## 7. References

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