Extended Abstracts of the 22nd (1990 International) Conference on Solid State Devices and Materials, Sendai, 1990, pp. 175-178

Thin Nitrided SiO_2 Films for EEPROMs

M. DUTOIT, E. GOIN, N. NOVKOVSKI[a], I. AIZENBERG[b],
J. MANTHEY* and J. SOLO DE ZALDIVAR*
Swiss Federal Institute of Technology,
CH 1015 Lausanne, Switzerland
* Faselec, CH 8045 Zurich, Switzerland

Two approaches for improving the electrical quality of thin SiO_2 films for EEPROMs are compared, i.e. rapid thermal processing (RTP) and plasma-assisted nitridation. The optimization of these processes and the resulting physical and electrical properties of thin oxynitride films are discussed. 1 kbit EEPROM arrays with an endurance of more than 10^6 cycles were fabricated with an industrial CMOS process.

1. INTRODUCTION

Even though EEPROMs have not become a large-volume commodity item yet, there is a need for such memories embedded in a wide variety of integrated circuits. The world-famous Swatch, for example, contains a few bits of non-volatile memory. As the thickness of the tunnel dielectric is reduced in modern technologies, it becomes crucial to control the endurance of EEPROMs, i.e. the maximum number of cycles they can be programmed before failure.

The goal of our work was to provide Flotox-type EEPROMs with a minimum endurance of 10^6 cycles in 1 kbit-size arrays. By experience, we found that to satisfy this requirement, individual cells need to last about 10 times longer.

Both RTP and plasma-assisted processing were evaluated to meet this goal. A methodology was devised to systematically optimize these processes without exploring the whole parameter space.

II PHYSICAL REQUIREMENTS

Two obvious questions that need to be answered before starting such an optimization are: 1) What method of characterization of thin dielectric films provides a representative estimate of their behavior in EEPROMs ? and 2) What is the optimum nitrogen profile and how does one achieve it ?

In our experience, endurance is limited by charge trapping, that is, memory window closing, rather than

---

[a] Present address: Physics Department, University of Skopje, pf 162, 91001 Skopje, Yugoslavia.

[b] Present address: Inst. of Probl. of Microelectron. Technol. and Superpure Mater., Acad. Sc. of the USSR, 142432 Chernogolovka, USSR

dielectric breakdown. Since these phenomena are correlated[1], either one can be used as an estimator of endurance. It is customary to measure the charge to breakdown Q_{BD} of an MOS capacitor under constant current stress. Yet, stressing with currents of both polarities or with pulses of alternate polarity is indispensable[2,3]. The peak current density during programming can reach several A/cm2. It is therefore advisable to measure Q_{BD} at comparable current levels.

One difficulty in optimizing the nitrogen profile is that very small concentrations need to be measured. We used the oxidation resistance of etched-back oxynitride films as an indication of the N concentration at the SiO_2/Si interface and observed that it is correlated with Q_{BD}[4]. It is maximized with a fairly light nitridation since a prolonged treatment will reoxidize the interface[5]. Nitrogen improves the resistance of the film to the generation of interface traps and improves Q_{BD} for both stressing polarities[6] (fig. 1).

III RAPID THERMAL PROCESSING

This is still the most popular technique for nitriding thin SiO_2 films[7]. Based on the considerations exposed in section II, we optimized a process with the results shown in fig. 2. Si-gate MOS capacitors were used in this study.

A process sequence that gave 10 nm - thick films with outstanding properties is the following: thermal oxidation at 1150 °C for about 10 s (lower temperatures yielded a higher defect density); nitridation in NH_3 at 1100 °C for 4 s; and reoxidation at 1150 °C for 60 s. The latter is indispensable for improving the electrical properties (interface charges as well as Q_{BD}). Its main role seems to be to drive out the H introduced during nitridation, although annealing in N_2, instead of reoxidation, yields poor results. In this respect, it would be interesting to replace NH_3 by other reactive gases that do not contain H, such as NF_3. This work is in progress in our laboratory.

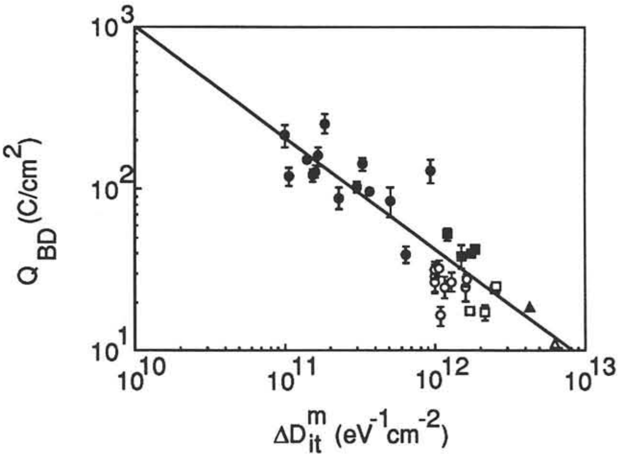

Figure 1 Charge to breakdown vs interface trap density generated after 5 C/cm^2 at J = ± 0.2 A/cm^2. (triangles: classical oxides, squares: RTP oxides, circles: oxynitrides, closed and open symbols: positive and negative gate stress, resp.)

Optimized films have a Q_{BD} of nearly 800 C/cm^2 at 10 mA/cm^2 and more than 40 C/cm^2 at 3 A/cm^2 (gate positive). Unfortunately, the improvement in the electrical properties achieved with RTP nitridation depends on gate polarity. This difference is ascribed to the asymmetrical role of nitridation in the prevention of interface trap generation[6].

EEPROMs with an optimized oxynitride injection layer were fabricated

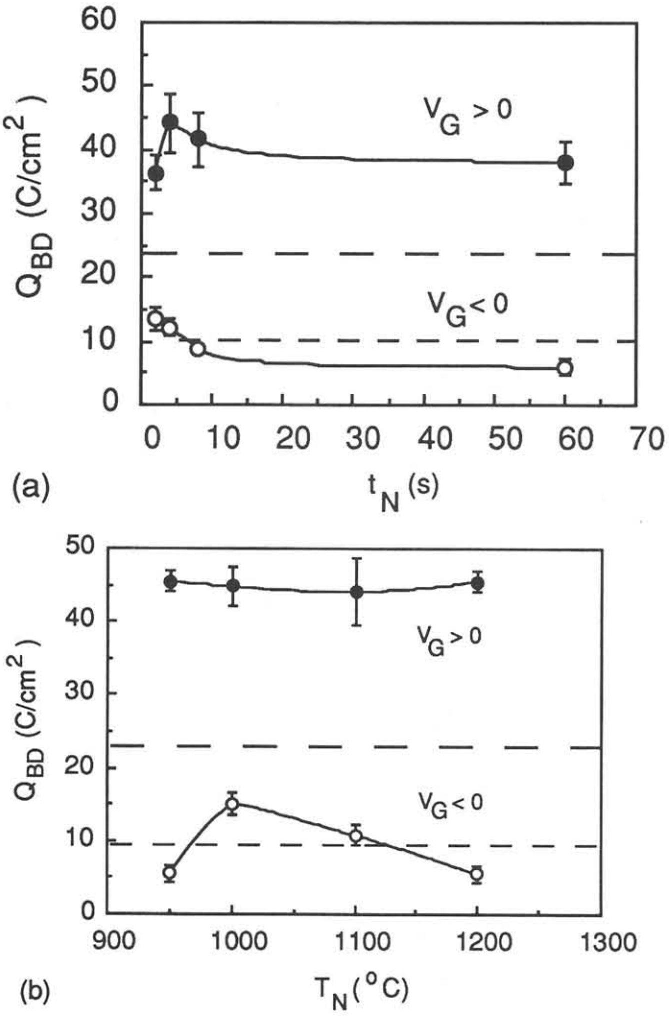

Figure 2 Influence of process parameters on Q_{BD} of 10 nm-thick RTP oxynitride films (J = ± 3 A/cm^2).
a) Variable duration of nitridation at 1100 °C; b) variable temperature of nitridation (optimum duration). Oxidation (10 s) and reoxidation (60 s) at 1150 °C. (dashed lines : oxide)

with an industrial 3 µm CMOS process8). Individual cells showed an endurance of more than 10^7 cycles (fig. 3), complete 1 kbit arrays well over 10^6 cycles. This is an order of magnitude better than the same devices incorporating a conventional oxide.

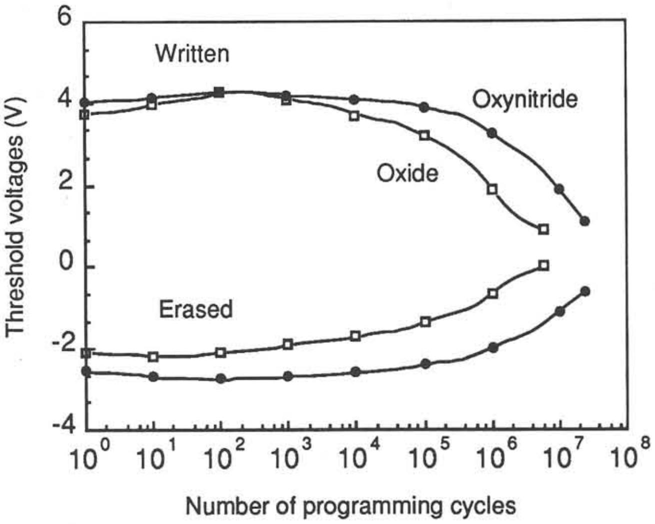

Figure 3 Endurance characteristics of two EEPROM cells: one with a furnace-grown oxide, the other with an optimized RTP oxynitride.

IV PLASMA-ASSISTED PROCESSING

The potential of plasma nitridation of thin SiO$_2$ films was established several years ago9). Its main advantage is to allow low-temperature processing. In previous work, we showed that the electrical properties of thin SiO$_2$ films can be improved by nitridation in a N$_2$ plasma without any additional heat treatment, probably because of the absence of H10). Yet, radiation damage seemed to be significant, so that temperatures of at least 700 °C were needed to anneal it out. In addition, the process window in which an improvement was achieved was rather narrow.

Here, we present new results on plasma nitridation of SiO$_2$ with rare gas-diluted N$_2$. This dilution modifies the concentrations of active species in the plasma and their kinetic energy on reaching the wafers11). It allows reduced processing temperatures.

Our plasma reactor incorporates a vertical quartz tube that is heated by a movable furnace12). Wafers are positioned on a multiple-electrode holder made of parallel, Si$_3$N$_4$-coated Ti plates. This configuration provides the advantage of efficient nitridation and batch processing.

For this study, Al-gate MOS capacitors were fabricated. Thin SiO_2 films nitrided in a 30 % N_2/Ar plasma are shown as an example (fig. 4). Even though an improvement over SiO_2 films is achieved without further heat treatment, the latter improves Q_{BD} even more. In this case (lightly doped p-type substrate), it was not possible to measure injection under positive gate polarity.

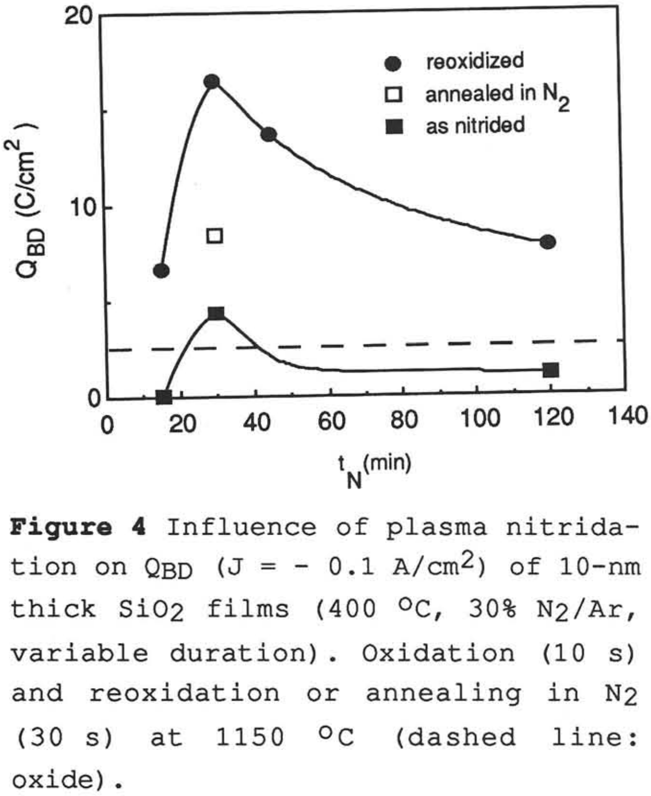

Figure 4 Influence of plasma nitridation on Q_{BD} ($J = -0.1$ A/cm^2) of 10-nm thick SiO_2 films (400 °C, 30% N_2/Ar, variable duration). Oxidation (10 s) and reoxidation or annealing in N_2 (30 s) at 1150 °C (dashed line: oxide).

V CONCLUSIONS

Our results show that a significant improvement in the endurance of EEPROMs can be obtained by RTP nitridation of the tunnel oxide under optimized conditions.

Even though RTP nitridation is close to industrial production, it still suffers from serious shortcomings, most prominent among them, temperature control, uniformity, reproducibility and throughput.

Plasma processing, which can be performed in batches in a traditional furnace at low temperatures, provides an interesting alternative. However, further work is needed to confirm our promising preliminary results with rare gas-diluted N_2.

REFERENCES

1) M. Dutoit, et al, **Appl. Surf. Science 30** (1987) 333.

2) P. Fazan, et al, **ECS Symp. Proc., 87-10** (1986) 398.

3) J. Manthey, et al, **Solid State Dev.**, G. Soncini and P.U. Calzolari ed., (North-Holland, Amsterdam, 1988) 269.

4) N. Novkovski, et al, **Appl. Phys. Lett. 54** (1989) 2408.

5) F.H.P.M. Habraken, et al, **J. Appl. Phys. 53** (1982) 6996.

6) N. Novkovski, et al, **Appl. Phys. Lett. 56** (1990) 2120.

7) T. Hori and H. Iwasaki, **IEEE EDL 9** (1988) 168.

8) R. E. Lüscher and J. Solo de Zaldivar, **ISSC Tech. Dig.** (1985) 260.

9) S. S. Wong and S. S. Oldham, **IEEE ED 32** (1985) 978.

10) P. Fazan, et al, **J. Vac. Sc. Technol. B 6** (1988) 1092.

11) D.V. Tsu and G. Lucovsky, **J. Vac. Sci. Technol. A 4** (1986) 480.

12) P. Fazan, et al, **Appl. Surf. Science 30** (1987) 224 .