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DEGRADATION OF MIOS MEMORY STRUCTURES

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Résumé. — L'étude comparative du décalage de fenêtre pendant le cycle d'écriture et d'effacement des systèmes MAOS et MNOS montre une forte dépendance par rapport à l'épaisseur du SiO_2 . Le système MNOS fait preuve d'une plus grande stabilité. La combinaison MANOS (recuissin à l'oxygène) est comparable à cet égard à celle de MNOS. Les résultats sur l'accroissement de la densité des états rapides de surface et sur la rétention des charges seront présentés. Les dates suggèrent que l'eau influence le phénomène de dégradation.

Abstract. — A comparative study of window shift during write/erase cycling of MAOS and MNOS devices shows strong dependence in the shift on SiO_2 thickness, the MNOS devices showing better stability. Their combination MANOS (O_2 annealed) is comparable in this respect to MNOS. Results on the increase of fast surface state density and on charge retention are reported. The data suggests that H_2O affects the degradation phenomena.

1. Introduction. — The attractive properties of Metal-Insulator- SiO_2 on Si (MIOS non-volatile memory devices for EAROM application) are partially offset by the degeneration of the memory under repeated write-erase operation [1]. This degeneration, a shift of the flat band voltage (V_{FB}) characterizing the two logical states of the device which define its memory window, takes place in the gate structure of the device. Thus it is of interest to investigate the MIOS-gate capacitor under repeated write-erase (w/e) cycling. Limiting the investigation to MIOS capacitors not only facilitates the sample preparation, but also simplifies a comparison to investigations on Negative Bias Stress (NBS) of MOS capacitors [2, 3, 4].

It has been reported that the degradation of MNOS memory devices is accompanied by an increase in the density of fast surface states (N_{ss}) and a reduced charge storage time [1]. For transistors a negative shift, of the threshold window [2, 3], for capacitors a positive shift of the flat band window [2, 4] has been observed. According to one proposal this shift is caused by the drift of OH groups in the thin SiO_2 layer and should be dependent on its thickness [4].

This paper will present data on a comparative study of this reliability problem for MNOS and MAOS structures and their dependence on the SiO_2 thickness. The reliability of the new MANOS structure [8] will be compared to that of MNOS and MAOS. The effect of O_2 annealing of Al_2O_3 on the reliability of MAOS and MANOS devices will be demonstrated.

2. Experimental. — **2.1 SAMPLE PREPARATION.** — MAOS and MNOS samples with SiO_2 layers of different thicknesses (between 1.2 and 5 nm) were fabricated. The oxidation of the $\langle 100 \rangle$ oriented $10 \Omega \text{ cm}$ silicon substrates was carried out in a mixture

of 10 % O_2 in N_2 at the deposition temperature of the next layer. The Si_3N_4 and Al_2O_3 layers were prepared pyrolytically at 900°C using the $\text{SiH}_4\text{-NH}_3\text{-H}_2\text{-N}_2$ and the $\text{AlBr}_3\text{-NO-H}_2\text{-N}_2$ systems respectively. MANOS capacitors were fabricated using the same technologies. Some of the MAOS and MANOS samples were annealed before metallization in a pure O_2 atmosphere for 15 min at the deposition temperature. Al dots were evaporated through a mask in an e-gun apparatus. Annealing of the Al contacts in N_2 for 15 min at 450°C concluded the fabrication process.

2.2 MEASURING SET-UP. — Wear-out measurements were carried out using an automatic system (Fig. 1); which measures the window shift of MIOS capacitors during w/e cycling. The w/e operation is interrupted periodically for a one second pause to measure and directly record the two V_{FB} values which define the logical window. The number of w/e cycles in which the window has shifted by an unacceptable amount will be designated as $Z'_{w/e}$ (see Fig. 2a). In this work, the

FIG. 1. — Block diagram of automatic measurement system for window shift.

FIG. 2. — Window shift (a) and N_{ss} change (b) of MAOS capacitors. Gate pulse cycle + 22 and - 42 V for 10 ms.

window size i.e. the difference between the two logical V_{FB} states, was chosen to be 5 V. This value is not only TTL compatible but also lies near the minimum retention margin of 4 V [10]. Along with the window shift measurement the density of the fast surface states N_{ss} was determined by the Gray and Brown method [9].

Before measuring the window degeneration or retention time of a virgin MAOS or MANOS capacitor it was stressed with negative pulses to saturate the electron injection from the metal electrode [11]. Otherwise the bistable states of the memory window will shift in positive direction due to this anomalous charging during erase operations. The magnitude of the positive shift depends on the erase pulse width.

The charge retention for the different structures was determined before and after performing the window shift measurements by checking the V_{FB} values as a function of storage time at room temperature. The samples were short-circuited before and after the V_{FB} check.

3. Results. — 3.1 RELATIONSHIP BETWEEN $Z'_{w/e}$, N AND SiO_2 THICKNESS. — The logical window for MAOS devices shifted in negative direction for repeated w/e cycling (Fig. 2a); in MNOS devices the shift was in opposite direction. Parallel with this shift N_{ss} on MAOS increases, as indicated in figure 2b. The increase in N_{ss} for MNOS devices is small in comparison and depends on the fabrication procedure : The

FIG. 3. — Number of write/erase cycles $Z'_{w/e}$ (constant window size) for MAOS and MNOS capacitors and different d_{SiO_2} ;

$$d_{\text{Si}_3\text{N}_4} = d_{\text{Al}_2\text{O}_3} = 84 \text{ nm} ;$$

write/erase pulse length 10 ms.

FIG. 4. — Density of fast surface states vs thickness of SiO_2 on MAOS-capacitors for constant initial SiO_2 field

$$E_{ox}^0 = 9.86 \text{ MV/cm} .$$

Parameter : $Z'_{w/e}$. Structure data : Al electrode, $d_{\text{Al}_2\text{O}_3} = 84 \text{ nm}$, d_{SiO_2} as indicated, p-Si substrate ; $10 \Omega \text{ cm}$.

TABLE I

	logical window shift	narrowing	$Z'_{w/e}$	N_{ss}^0 cm^{-2}	ΔN_{ss} cm^{-2}
MNOS	pos.	no	Fig. 3	5×10^{10}	$\leq 2 \times 10^{10}$
MAOS	neg.	yes	Fig. 3	5×10^{10}	$< 10^{12}$
MAOS (O_2)	neg.	yes	as in MAOS	5×10^{10}	$< 10^{12}$
MANOS	neg.	yes	as in MAOS	1×10^{11}	$< 10^{12}$
MANOS (O_2)	pos.	yes	as in MNOS	1×10^{11}	$< 10^{12}$

increase for capacitors on which oxide growth and nitride deposition were carried out *in situ* was very small ($\Delta N_{ss} \leq 2 \times 10^{10}$), for devices fabricated in separate oxidation and deposition furnaces the increase was somewhat larger ($\Delta N_{ss} \leq 1 \times 10^{11}$). From figure 3, $Z'_{w/e}$ may be seen to become larger for thinner SiO_2 layers; this thickness dependence is more pronounced for MNOS than for MAOS devices. The larger increase in N_{ss} for thicker SiO_2 films is not simply caused by the larger field required for erasure in these cases: figure 4 shows that the effect also occurs at fixed value of the initial field across the SiO_2 ($E_{0,x}^0$). MANOS devices (the insulator structure was prepared in three separate furnaces) behave like MAOS structures with regard to window shift and N_{ss} . A summary of these results is presented in table I.

3.2 EFFECT OF O_2 ANNEALING IN MAOS AND MANOS. — MAOS capacitors with 2.5 nm of SiO_2 and 84 nm of Al_2O_3 on p-Si substrates were annealed in O_2 at the deposition temperature for times from 5 to 30 min. This treatment causes the minimum positive gate voltage required for negatively charging (*write threshold*) to increase; the opposite « erase threshold » remains unaffected. $Z'_{w/e}$ drops off exponentially with annealing time in O_2 . For a 15 min, anneal this effect amounts to 2 decades.

On the other hand, O_2 annealing of a MANOS structure with 2.5 nm of SiO_2 , 20 nm of Si_3N_4 and 60 nm of Al_2O_3 was found to reduce both thresholds and make the write-erase voltages more symmetrical. The window shift for repeated write-erase cycling is positive and comparable to that for MNOS devices. However, in the MANOS case there is a clear increase in N_{ss} .

3.3 WINDOW RECOVERY. — The positive window shift in MNOS and O_2 annealed MANOS devices recovers when interrupting the write/erase operation. In fact, already during the pause required for reading a perceptible recovery is observed. The $Z'_{w/e}$ values in table I were obtained for 20 readings per decade of $Z_{w/e}$. Complete recovery at room temperature requires times in the order of 10 min.

For MAOS and unannealed MANOS devices recovery of the window and elimination of ΔN_{ss} requires

an annealing treatment in N_2 or room air above room temperature. As an example, complete recovery occurs in 15 min at 200 °C, in 45 min, at 120 °C.

3.4 CHARGE RETENTION. — Charge retention measurements for the larger positive logical V_{FB} state before and after applying $Z'_{w/e}$ write-erase pulses gave the following results: For MNOS no change was detected, for MAOS (unannealed) and MANOS (unannealed) a very slight deterioration and for MAOS (O_2 -annealed) a somewhat larger degradation. Surprisingly, for MANOS (O_2 -annealed) the V_{FB} value, which before annealing decreased with time, increased very slightly with time after write-erase cycling.

4. Discussion. — From our data it is clear that the maximum tolerable number of w/e cycles depends on the nature of the structure. Thicker SiO_2 films lead to decreased $Z'_{w/e}$ values. The largest values were obtained for MNOS and O_2 -annealed MANOS devices. The data for annealed and unannealed MANOS devices indicate that there is no inherent relation between window shift and ΔN_{ss} . The more rapid degradation of MAOS devices may be caused by the larger erasure fields.

MNOS devices with the double insulator prepared in one furnace without exposing the SiO_2 film to room ambient exhibit the smallest ΔN_{ss} values. This finding and the (predicted) dependence on SiO_2 thickness suggests that water (OH groups) does indeed play a role in the creation of fast surface states. The larger ΔN_{ss} values for MAOS would follow from the relatively large water pressure in the Al_2O_3 deposition process. Although the SiO_2 layer in the MANOS structures had been exposed to room ambient the large increase in N_{ss} would require that additional OH had penetrated through the Si_3N_4 during Al_2O_3 deposition. However, the present data do not permit to draw definitive conclusions on this topic.

From an overall point of view, it appears that MNOS and O_2 annealed MANOS devices present the most favorable combination of properties. Particularly in the latter case it may be expected that continued technological studies will lead to further improvement in their behavior.

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