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MAOS NON-VOLATILE MEMORY STRUCTURES WITH LOWER BANDGAP STORAGE LAYER

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Résumé. — L'introduction d'une couche mince de Si_3N_4 dans la structure de mémoire MAOS (métal, Al_2O_3 , SiO_2 , Si) augmente le stockage des charges dans la mémoire et réduit les voltages d'inscription pour cette structure MANOS. La recuisson à l'oxygène agit d'une manière significative sur ces propriétés et sur le mécanisme de chargement. Des résultats préliminaires sur la rétention de la charge seront présentés.

Abstract. — Introduction of a thin Si_3N_4 layer in metal- Al_2O_3 - SiO_2 -Si (MAOS) memory structures leads to increased charge storage capability and reduced writing voltages for these MANOS structures. O_2 annealing significantly affects these properties and the charging mechanism. Preliminary results on charge retention are presented.

1. Introduction. — Writing and erasure of non-volatile field effect memory devices with a layered dielectric storage medium takes place primarily by tunneling of charge carriers from the silicon into the conduction or valence band of the outer insulator, or by the reverse process. Because of its unsurpassed dielectric properties thermally grown SiO_2 is the logical and nearly unavoidable choice for the inner insulator of the dual dielectric gate system. The need for low writing voltages would dictate that the second insulator of the metal-insulator- SiO_2 -Si combination have a relatively modest bandgap (to reduce the tunneling barrier) and high dielectric constant ϵ (to increase the relative field strength across the SiO_2). On the other hand, suppression of the undesirable charge injection from the metal electrode demands a high internal barrier, necessitating the use of a large bandgap material. These conflicting requirements are best met by using a three layer system [1, 2] containing a thin storage layer in addition to the high ϵ - large bandgap outer insulator. Kahng and Sze's original device with a thin metal storage film [3], that of Laibowitz and Stiles with small metal particles [4], Horiuchi's structure with Si particles [5] as well as Shuskus' HfO_2 - HfN - SiO_2 system [6] belong to this category. Closely related is the MAOS device investigated by Kahng *et al.* into which deep traps were introduced at the Al_2O_3 - SiO_2 interface by doping with W [7] or WO_3 [8].

In the present paper we will introduce a three layer memory structure which can be fabricated using standard technology and avoids the charge retention problems encountered with metal interlayers. Our gate system is basically a MAOS structure with Si_3N_4 storage layer ; we will designate it as MANOS structure. It combines the advantages of the high

dielectric constant of Al_2O_3 (9.0 vs 6.2 for Si_3N_4) with those of the lower band gap of Si_3N_4 (5.1 eV vs 8.7 eV for Al_2O_3). The band diagram in figure 1, which has been composed of the data available for the barriers between the components [1], clearly indicates the potential wells for electrons and holes between the SiO_2 - Si_3N_4 and Si_3N_4 - Al_2O_3 barriers. We will show that the introduction of this nitride layer increases the amount of charge stored for a given gate voltage and reduces the voltage required to charge the insulator system to a given level.

FIG. 1. — Energy band diagram for MANOS structure.

2. **Experimental.** — MANOS capacitors with various Si_3N_4 thicknesses (including the limiting case MAOS) were fabricated by oxidizing $\langle 100 \rangle$ oriented $1\ \Omega\text{ cm}$ silicon substrates in 10 % O_2/N_2

followed by deposition of Si_3N_4 from a 0.1 % $\text{NH}_3/1.4 \times 10^{-2}$ % $\text{SiH}_4/10$ % H_2/N_2 mixture and of Al_2O_3 from a 0.26 % $\text{AlBr}_3/2$ % $\text{NO}/10$ % H_2/N_2 mixture in different resistance heated furnaces, all at 900 °C. In order to study the effects of subsequent high temperature treatments, a number of samples were annealed in O_2 or N_2 , also at 900 °C. Metallization was carried out by evaporating Al from an e-gun apparatus through a mask onto the dielectric system. A 15 min. anneal in N_2 at 450 °C concluded the fabricating cycle.

Film thicknesses were measured ellipsometrically. The Al_2O_3 layers were polycrystalline (crystallite size : approx. 10 nm) with refractive index 1.75 [8]. For the Si_3N_4 films a value of 1.95 was obtained.

The charge condition of the samples was determined from standard high frequency C-V measurements. To obtain realistic conditions the devices were cycled back and forth between the logical states before measuring. The data were obtained by switching from one of these states towards the other.

3. Results and discussion. — When introducing thin Si_3N_4 layers in the MAOS structure the charge uptake for a given pulse height and length increases, as evidenced by the increased magnitude of the logical window (difference between the flatband voltages V_{FB} for positive and negative gate polarity) in figure 2. The magnitude of the increase depends on the pulse length and is larger for O_2 annealed samples. To facilitate a comparison with other systems the gate voltage has been expressed in terms of the field across the thin SiO_2 film (E_{ox}^0) in the absence of stored charge. The data for a MNOS capacitor with

FIG. 2. — Dependence of V_{FB} on thickness of Si_3N_4 layer for MANOS capacitors. $E_{\text{ox}}^0 = 10 \text{ MV cm}^{-1}$. Data for MAOS and MNOS ($d_n = 50 \text{ nm}$) are also shown. Parameter : pulse length ; $d_{\text{ox}} = 2.5 \text{ nm}$ in all cases ; $d_{\text{Al}_2\text{O}_3} = 70 \text{ nm}$.

the same SiO_2 thickness and total capacitance equal to that of the MAOS structure (i.e. with $d_n = 0 \text{ nm}$) are also indicated.

Figure 3 shows the E_{ox}^0 values required to obtain in 2 min V_{FB} values of +5 and -5 V, again for the same range of d_n . Interestingly, the unannealed and O_2 annealed samples behave in a different manner. The unannealed structures require the larger fields to obtain this 10 V window. More important, for the unannealed samples E_{ox}^0 decreases in a pronounced fashion with increasing d_n for the negative V_{FB} value, but only very weakly for the positive V_{FB} value. This behaviour, which was not affected by heating in N_2 , may be seen to occur for the opposite V_{FB} polarities upon O_2 annealing.

FIG. 3. — Fields E_{ox}^0 required for obtaining $\pm 5 \text{ V}$ shift in V_{FB} for unannealed and O_2 annealed MANOS capacitors ; $d_{\text{ox}} = 2.5 \text{ nm}$; $d_{\text{Al}_2\text{O}_3} = 70 \text{ nm}$.

We propose that these observations may be explained as follows : the minimum field across the SiO_2 layer required for injection of electrons into the conduction band of the nitride may be shown (Fig. 4) to decrease with increasing thickness (d_n) of the nitride layer :

$$E_{\text{ox}}^0(\text{min}) = (\varphi_1 - \varphi_2) (d_{\text{ox}} + d_n \varepsilon_{\text{ox}}/\varepsilon_n)^{-1} \quad (1)$$

Upon injection in the conduction band the carriers will move over some distance until they become trapped. Since the $\text{Si}_3\text{N}_4\text{-Al}_2\text{O}_3$ barrier tends to confine the carriers to the nitride layer, the storage capability at a given E_{ox}^0 value should increase with d_n . Fields below $E_{\text{ox}}^0(\text{min})$ would only allow injection into the conduction band of the Al_2O_3 or into

FIG. 4. — Minimum field required for electron injection in Si_3N_4 layer of MANOS structure.

traps in this material [9]. In this case the tunneling probability and consequently the charging rate should be considerably reduced. Assuming that the rate of the reverse process is determined by the tunneling of electrons through the SiO_2 layer one would again expect a low discharging field, but no dependence on d_n .

The O_2 annealed MANOS capacitors apparently follow this pattern where electrons are the dominant carriers. The low conductivity of O_2 annealed Al_2O_3 [9] tends to confine the electrons to the nitride layer, which would make the model eminently applicable.

The opposite behavior of the unannealed samples would indicate that in this case holes play an important role in the charging process. For holes the barrier structure of the system is qualitatively the same as for electrons and one expects an equation similar to (1) to hold. Under negative bias electrons are injected at the Al gate, thereby increasing simultaneously the Al- Al_2O_3 barrier towards electron injection and the field at the Si- SiO_2 interface. Thus the rate of hole injection into the Si_3N_4 is increased [10]; also because of their proximity to the silicon the effect of the positive charges ultimately appears to dominate. It is known, that only in unannealed Al_2O_3 the electron injection from Al plays an important role [11]. In discharging the effect of the negative charge in the Al_2O_3 has to be overcome, which requires relatively large fields.

The preliminary charge retention data for MANOS capacitors in figure 5 show that the unannealed

FIG. 5. — Normalized charge loss (room temp.; short circuit) for MANOS ($d_n = 20$ nm), MNOS and MAOS capacitors; $d_{ox} = 2.5$ nm in all cases.

structures hold positive charges (V_{FB} neg.) better than negative ones; in this respect they are comparable to MNOS; MAOS devices exhibit the opposite behavior. Upon O_2 annealing the retention capability of MANOS for positive charge decreases to the level for negative charge.

4. Conclusions. — The data in this paper demonstrate the interesting properties of the MANOS structure. These properties are most easily explained for the O_2 annealed devices, where the charge storage is mainly determined by the Si_3N_4 layer. In this case electrons are the major carriers. The unannealed structures behave in a more complicated fashion. Here hole injection into the Si_3N_4 also appears to play a role. In both cases the writing voltages are reduced by the addition of the nitride layer. Equating the behavior of MANOS devices with that of MNOS [12] appears to be an oversimplification.

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