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► **To cite this version:**

M. Severi, M. Impronta, L. Dori, S. Guerri. PROCESS DEPENDENCE OF HOLE TRAPPING IN NITRIDED SiO₂ FILMS. Journal de Physique Colloques, 1988, 49 (C4), pp.C4-417-C4-420. 10.1051/jphyscol:1988488 . jpa-00227986

HAL Id: jpa-00227986

<https://hal.science/jpa-00227986>

Submitted on 4 Feb 2008

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PROCESS DEPENDENCE OF HOLE TRAPPING IN NITRIDED SiO_2 FILMS

M. SEVERI, M. IMPRONTA, L. DORI and S. GUERRI

CNR, Istituto LAMEL, Via de' Castagnoli n.1, I-40126 Bologna, Italy

Résumé - On a effectué une analyse systématique du piégeage des trous dans des couches minces (20-30 nm) d'oxyde nitruré avec la technique de l'injection à avalanche, en fonction des conditions de nitruration. La nitruration réalisée à températures relativement basses (700-800°C) et pour des temps courts produit une augmentation des pièges des trous. La réduction du piégeage des trous peut être obtenue seulement avec des conditions de nitruration plus sévères. On a étudié aussi l'effet du recuit en atmosphère d'oxygène après nitruration.

Abstract - A systematic investigation of hole trapping in 20-30 nm nitrided oxides as a function of the nitridation conditions were performed using the avalanche injection technique. Nitridation carried out at relatively low temperatures (700-800°C) and for short times brings about an increase of hole traps. Hole trapping reduction can only be achieved for more severe nitridation conditions. The effect of postnitridation annealing in oxygen was also studied.

1 - INTRODUCTION

Thermally nitrided SiO_2 films are being extensively investigated in order to improve several properties of the insulator in metal-oxide-semiconductor structures for VLSI. In particular, it has been inferred from high field stress that hole traps in nitrided oxides are reduced to very low levels /1/. Very recently /2/, this has been confirmed by direct measurements using hole avalanche injection. By using the same technique, in this work we have performed a systematic investigation of hole trapping in 20-30 nm nitrided oxides as a function of the nitridation conditions and postnitridation annealing treatments.

2 - EXPERIMENTAL

n-type (100)-oriented silicon substrates with a resistivity of 0.1 ohm.cm were used. 20-30 nm gate oxide films were thermally grown in dry oxygen at 1000°C in quartz-tube furnace and in-situ annealed at the same temperature in N_2 for 10 min. Thermal nitridation was carried out in ultrapure ammonia gas at temperatures between 700 and 1100°C and for times ranging from 5 to 60 min in a cold-wall rf-heated reactor at atmospheric pressure. Some of the nitrided oxides were subsequently annealed in oxygen at 900-1000°C. Aluminum and gold were deposited by evaporation. Electrodes with areas of 2.46×10^{-3} cm² were formed by photolithography or using a metal mask. In some Al-gate samples, a post metallization anneal (PMA) in nitrogen at 450°C for 20 min was performed. Avalanche injection was achieved with a 150-kHz sawtooth signal. The average injected current density was kept constant at a value of 1.2×10^{-7} A/cm². All the measurements were done at room temperature. The oxide charge buildup was monitored by periodically interrupting the injection and performing C-V measurements.

3 - RESULTS AND DISCUSSION

Let us first discuss some experimental results obtained on standard SiO_2 films. Fig.1 shows the negative flatband voltage shift upon hole injection for Al and Au gate capacitors with 30 nm SiO_2 . Two features are worth noticing: a) Au and Al gate capacitors before PMA show very similar hole trapping behavior. This result rules out that electron injection from the gate gives a significant contribution to the voltage shift. b) PMA treatment reduces hole trapping in Al gate samples. This result is in agreement with some indications already reported in the literature without discussion /2-4/. On the other hand, hole trapping in Au gate samples does not practically change by performing an anneal in forming gas before metallization. It is our opinion that the effect of PMA is related to the modification of the stress at the SiO_2/Si interface brought about by the PMA itself. Upon cooling to room temperature, thermal mismatch leads to a large tensile stress in the Al film /5/ which counteract the compressive stress in the SiO_2 . In this way, the density of the strained Si-O-Si bonds near the Si/SiO_2 interface

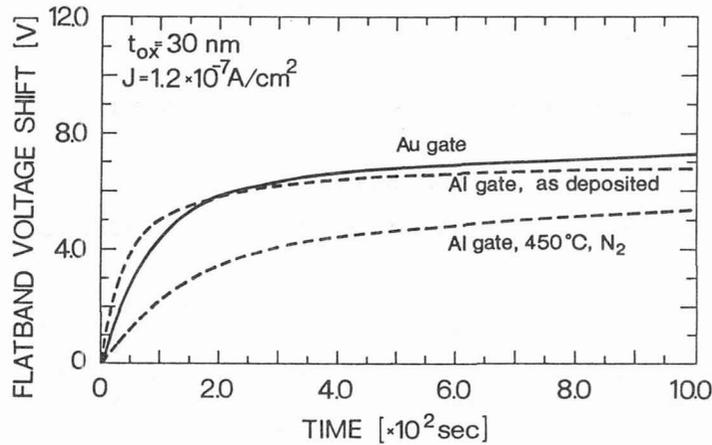


Fig.1 - Negative flatband voltage shift by avalanche injection of holes in 30 nm SiO_2 with as deposited Al (dashed curve) and Au (solid curve) gate. For Al, data are also shown after PMA.

might be reduced. Strained bonds near the interface have been suggested as one of the defects which can give rise to hole traps /3/. The possibility that mechanical stress in Al gate might reduce the strained bonds was first proposed by Chin and Ma /6/ in discussing the generation of interface states by ionizing radiations.

Now we turn to discuss the trapping properties of the nitrated oxides with Au gate electrodes. Similar results were obtained in Al gate samples. Fig.2 shows the effect of the nitridation temperature from 700°C to 1100°C on the hole trapping in 30 nm SiO_2 films.

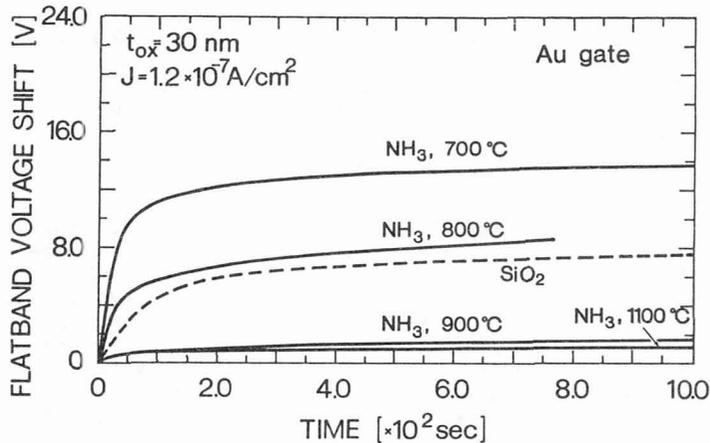


Fig.2 - Effect of nitridation temperature on the hole trapping in 30 nm SiO_2 with Au gate. Nitridation time was 30 min. Dot area = 2.46×10^{-3} cm².

As can be seen, nitridation at 700 and 800°C increases hole trapping with respect to the standard oxide, while at higher temperatures a remarkable decrease is obtained. We believe that the effect on hole trapping is strictly related to the nitridation kinetics /7,8/. For low nitridation temperatures (700-800°C) and/or for short times, there is a pile up of nitrogen at the Si/SiO₂ interface. In these conditions, hole traps increase. However, when the nitridation process is carried out at higher temperatures and/or for longer times, the nitrogen peak moves away from the interface and an oxygen-rich layer grows. The formation of this layer has been attributed to the oxygen released by the exchange reaction in the bulk of the oxide /8/. This oxygen may help in reducing the oxygen deficiency near the Si/insulator interface which has been suggested to be one of the cause for hole traps /9/. To test this hypothesis we have performed some experiments by varying the nitridation time at

a fixed temperature (900°C). The results are reported in Fig.3. For a short nitridation time, hole trapping steeply increases, in correlation with the rapid increase of the nitrogen concentration at the Si/dielectric interface. With increasing nitridation time, oxygen diffuses to the interface and the hole traps decrease. It is interesting to note that saturation has been observed for a 60 min nitridation.

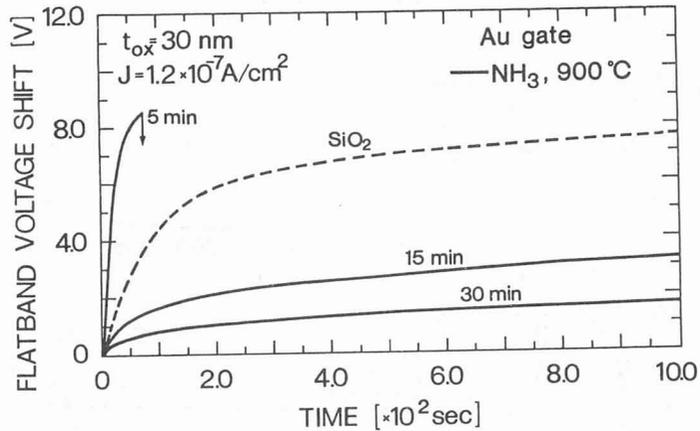


Fig.3 - Effect of nitridation time on the hole trapping in 30 nm SiO_2 with Au gate. Nitridation temperature was 900°C. The arrow indicates breakdown.

A decrease in the strain in the interfacial region with the increase of nitrogen, as already suggested /2/, may give a further contribution to the reduction of the hole trap density. The reduction of the hole traps brings about a reduction of the interface states generated upon avalanche injection of holes, as can be seen in Fig.4, which shows quasi-static C-V curves after 100 sec of injection for pure oxide and for oxides nitrided at 900°C for 30 min. These results confirm those reported in /2/.

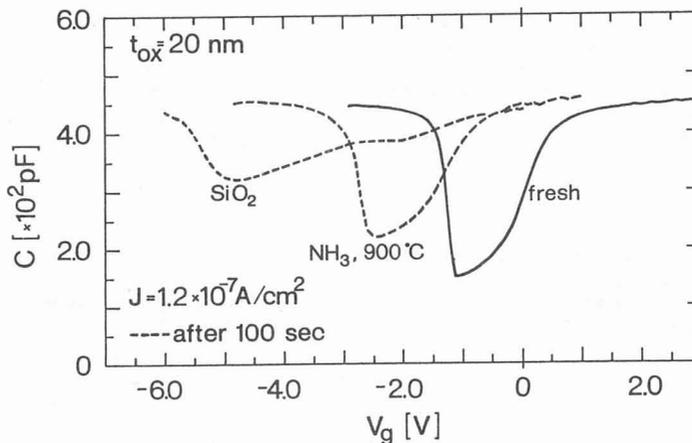


Fig.4 - Quasi-static C-V curves for 20 nm SiO_2 and for nitrided oxide after 100 sec of hole injection with a current density of $1.2 \times 10^{-7} \text{ A/cm}^2$.

It is interesting to observe that similarities and differences exist between hole and electron trapping in nitrided oxides. Contrary to hole traps, electron traps increase with the nitridation temperature /10/; however, an interfacial phenomenon, like the "anomalous positive charge" (APC) generation during electron avalanche injection, shows the same nitridation temperature and time dependence as hole trapping, suggesting a possible correlation between trapped holes and APC.

Finally, we would like to discuss some preliminary results on the effect of postnitridation heat treatments. The dependence of hole trapping on high temperature annealings in oxygen is

illustrated in Fig.5 for oxides nitrated at 900°C. It can be seen that hole trapping increases dramatically for the annealing at 950°C for 15 min, while it gradually decreases by performing more severe oxidizing treatments. Eventually, for a 60 min annealing at 1000°C a hole trapping lower than that in as-nitrated oxides is obtained. The increase in the hole trapping is probably due to the extension of the strained-bond region towards the oxide bulk through a viscous flow process during the anneal at high temperature ($\geq 950^\circ\text{C}$) /3,4/. Only when oxygen succeeds in penetrating the SiON barrier and reaches the interface, the hole traps can be reduced.

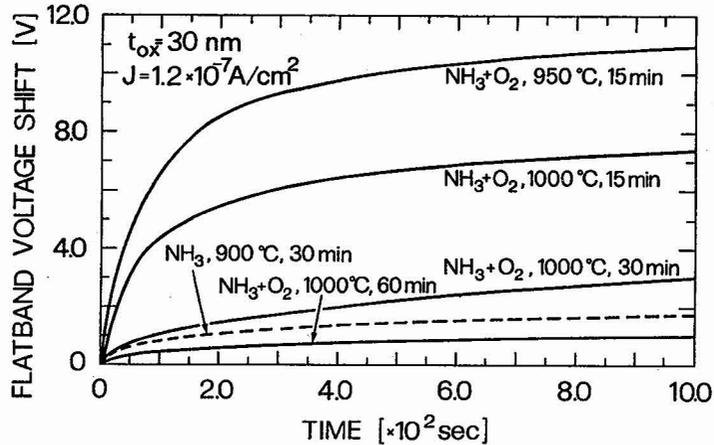


Fig.5 - Effect of postnitridation heat treatments in oxygen on the hole trapping in 30 nm SiO_2 nitrated at 900°C for 30 min.

4 - CONCLUSIONS

We have found that hole trapping in nitrated oxides depends on the nitridation conditions and on the postnitridation heat treatments. A reduction of hole trapping can only be achieved for relatively severe nitridation conditions (temperature $\geq 900^\circ\text{C}$ and time > 15 min). This reduction has been correlated with the formation of an oxygen-rich layer near the Si/insulator interface. A postnitridation O_2 anneal can increase or decrease the hole traps: its effect depends critically on the temperature and time of the process.

ACKNOWLEDGEMENTS

The authors would like to thank P.Negrini, P.Castelli and G.Pizzochero for their assistance in sample preparation and M.Rancoita for avalanche measurements. This work has been supported by the Progetto Finalizzato "Materiali e Dispositivi per l'Elettronica allo Stato Solido" of the Consiglio Nazionale delle Ricerche, Roma.

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