

# RADIATION EFFECT ON FLUORINATED SiO<sub>2</sub> FILMS

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## ABSTRACT

A systematic investigation of  $\gamma$  radiation effects in gate SiO<sub>2</sub> as a function of the fluorine ion implantation conditions was performed. It has been found that the generation of interface states and oxide trapped charges in fluorinated MOSFETs depends strongly on implantation conditions. The action of F in oxides is the conjunction of positive and negative effects. A model by forming Si-F bonds to substitute the other strained bonds which easily become charge traps under irradiation and to relax the bond stress on Si / SiO<sub>2</sub> interface is used for experimental explanation.

**Keywords** Threshold voltage, Oxide trapped charge, Interface state, Radiation

## 1 INTRODUCTION

It has been reported that by incorporating minute amounts of fluorine in thermal SiO<sub>2</sub> the interface radiation hardness can be improved<sup>[1-13]</sup>. For example, fluorine was introduced by HF surface treatment of the Si wafer prior to oxidation<sup>[1-3]</sup>, or by admitting minute amount of NF<sub>3</sub> at the initial stage of oxidation<sup>[11-13]</sup>, or by low F<sup>+</sup> implantation onto the layer of the polysilicon gate electrode<sup>[5-10]</sup>. So far little investigation on process influences, however, has systematically been made. Therefore the  $\gamma$  irradiation responses of MOSFET's for different surface, energy, doses and annealing technologies of F<sup>+</sup> implantation are systematically investigated. It has been found that the acts of F in oxides and the radiation responses are restricted strongly by the conditions of F<sup>+</sup> implantation.

## 2 EXPERIMENTAL

The P-channel and N-channel MOSFET used in this study were fabricated on (100) n-type silicon substrate of 3-4.5  $\Omega \cdot \text{cm}$ . The gate films were grown in dry O<sub>2</sub> or H<sub>2</sub>+O<sub>2</sub> to a thickness of 50 nm, followed by annealing in N<sub>2</sub> at 900°C. The thickness of polycrystalline film was 500 nm, and the poly-Si gate area was defined photolithographically.

The processing details of fluorinated oxides are described below.

a. F ions with 43 keV were implanted into the dry oxide or the upper layer of the

polysilicon gate before and after the polysilicon deposition, respectively.

b. Either 43 keV or 30 keV F ions were implanted onto the upper polysilicon layer of dry oxide.

After above steps all devices were annealed at 900°C in N<sub>2</sub>.

c. F ions with 30 keV were introduced into the upper layer of polysilicon gate, then followed by annealing at 900°C and 950°C in N<sub>2</sub>, respectively.

A  $I-V$  subthreshold technique was adopted to analyze the dependence of threshold voltage shifts, oxide trapped charge and interface state densities on F<sup>+</sup> implantation processes.

Irradiation was carried on <sup>60</sup>Co source. The dose rate was 2 Gy(Si) / s. The threshold voltage was obtained by  $I_{ds}-V_{gs}$  curves ( $I-V$  curves for short) and the densities of oxide trapped charges and interface states were calculated by subthreshold method<sup>[14]</sup>. The threshold voltage shifts induced by oxide trapped charges and interface states were obtained by stretch out principle<sup>[15]</sup>. All measurements were completed in 30 min.

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Implantation layer

The threshold voltage shifts induced by oxide trapped charges ( $\Delta V_{ot}$ ) and interface states ( $\Delta V_{it}$ ) under irradiation for PMOSFET implanted F<sup>+</sup> before and after polysilicon deposition are shown in Figs.1 and 2, respectively. F<sup>+</sup> dose is

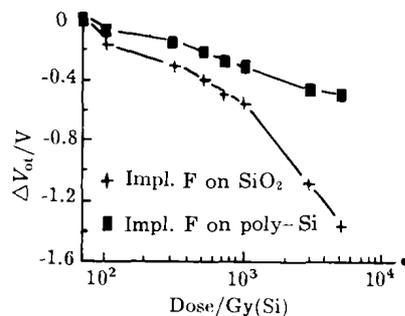


Fig.1  $\Delta V_{ot}$  vs dose for PMOSFET

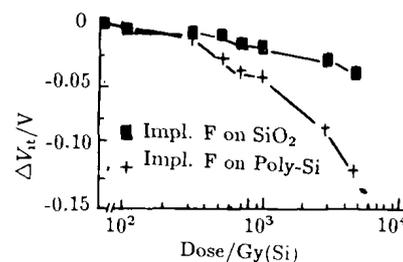


Fig.2  $\Delta V_{it}$  vs dose for PMOSFET

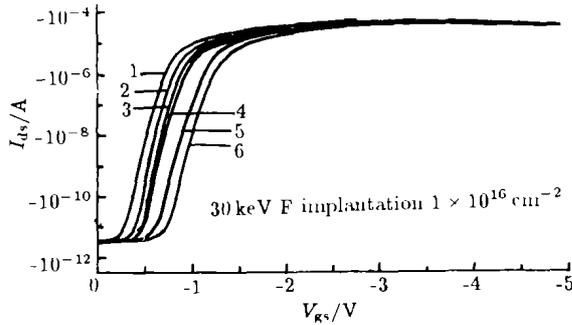
$5 \times 10^{15} \text{ cm}^{-2}$  with irradiation bias  $V_{gs} = 0 \text{ V}$ . It is seen that both  $\Delta V_{ot}$  and  $\Delta V_{it}$  for polysilicon layer implantation are smaller than that for SiO<sub>2</sub> layer implantation. In other words, the former has more resistant to radiation damages than the latter.

The purpose of post-implantation annealing is to diffuse F into the gates SiO<sub>2</sub> toward the Si / SiO<sub>2</sub> interface, to reduce the defects induced by F ion implantation, to enhance the incorporation of F and Si bonds for the substitution of Si-H, Si-OH, or Si-O strained bonds. Under identical implantation energy and annealing the gate dielectrics damage for SiO<sub>2</sub> layer implantation is more critical than that for

polysilicon layer implantation, and for former less F ions are left in SiO<sub>2</sub> gate oxide with less opportunities to substitute strained bonds because many F ions are pushed into Si substrate.

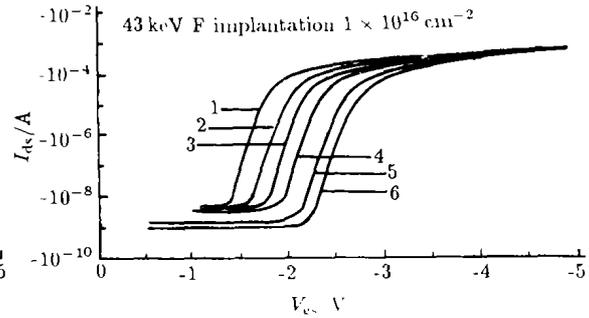
**3.2 Fluorine implantation energy**

$I_{ds}-V_{gs}$  radiation responses for 30 keV and 43 keV F<sup>+</sup> implantation were described in Figs.3 and 4, respectively. Radiation bias is  $V_{gs}=-5V$  with F<sup>+</sup> dose  $1 \times 10^{16} \text{ cm}^{-2}$ . The data manifest that the negative shift and distortion of  $I_{ds}-V_{gs}$  curves with radiation doses for 30 keV F<sup>+</sup> implantation is less than that for 43 keV implantation.



**Fig.3** The  $I_{ds}-V_{gs}$  curves of a PMOSFET for 30 keV F<sup>+</sup> implantation as a function of dose

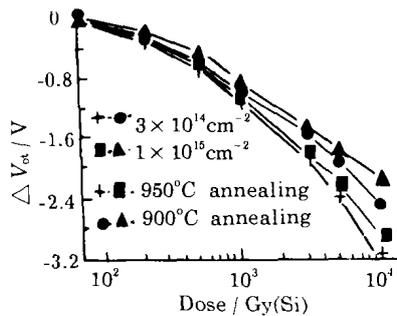
1: initial 2: 200 Gy 3:500 Gy 4:1000 Gy 5:3000 Gy 6:5000 Gy



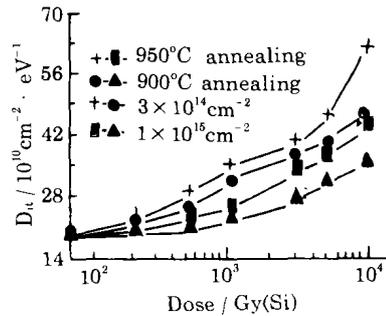
**Fig.4** The  $I_{ds}-V_{gs}$  curves of a PMOSFET for 43 keV F implantation as a function of dose

The larger negative shift and distortion of  $I_{ds}-V_{gs}$  curves are attributed to the more radiation-induced oxide trapped charges and interface states. So that there is only less radiation-induced charges accumulation for 30 keV F<sup>+</sup> implantation. The suppression is less significant in 43keV fluorinated oxide than in 30keV one due to larger amount of defects induced by F<sup>+</sup> implantation.

**3.3 Post-implantation annealing**



**Fig.5**  $\Delta V_{ot}$  vs radiation dose



**Fig.6**  $D_{it}$  vs radiation dose

Fig.5 and 6 show the threshold voltage shifts due to the oxide trapped charges and the interface states induced by  $\gamma$  irradiation as a function of total doses for

PMOSFETs with two annealing conditions (in N<sub>2</sub> at 900°C and 950°C, respectively). It is evident that the generation of oxide trapped charges and interface states for 900°C annealing is suppressed much more because the optimum annealing conditions result in the smaller amount of implantation defects.

### 3.4 F<sup>+</sup> doses

Figs.7 and 8 show the density increase of radiation-induced oxide trapped charges and interface states,  $\Delta N_{ot}$  and  $\Delta D_{it}$ , as a function of F<sup>+</sup> dose. Fluorine has been introduced into pyrogenic gate oxide through polysilicon films by low energy (30 keV) F<sup>+</sup> implantation and subsequent annealing at 900°C in N<sub>2</sub>. Irradiation bias is  $V_{gs} = 0$  V. The results in figures suggest that the  $\Delta N_{ot}$  and  $\Delta D_{it}$  are reduced for fluorinated MOSFETs in the dose range  $5 \times 10^{14} - 2 \times 10^{16} \text{ cm}^{-2}$ , as compared with the control thermal oxides, with significant improvement of interface hardness around  $1 \times 10^{16} \text{ cm}^{-2}$ . When the F<sup>+</sup> dose exceeds  $2 \times 10^{16} \text{ cm}^{-2}$ , a substantial increase of trapped charges occurs and the little improvement of radiation hardness occurs as low as  $5 \times 10^{14} \text{ cm}^{-2}$ .

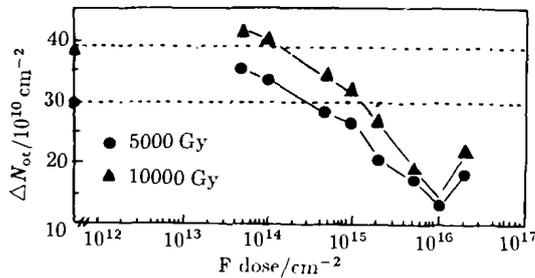


Fig.7  $\Delta N_{ot}$  vs F<sup>+</sup> dose

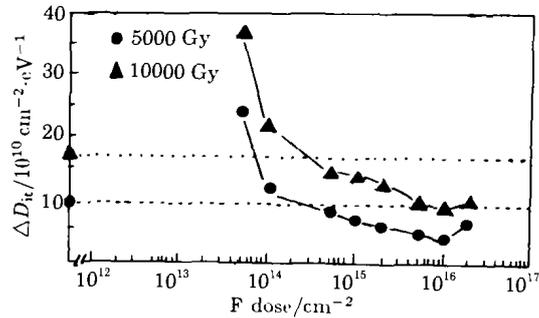


Fig.8  $\Delta D_{it}$  vs F<sup>+</sup> dose

From these results it can be concluded that an optimum fluorine concentration corresponds to an implantation dose in the range  $5 \times 10^{14} - 2 \times 10^{16} \text{ cm}^{-2}$ . Weak or little radiation improvement responds to heavy (excessive) or light (inadequate) amount of F<sup>+</sup> doses.

Positive and negative effects are the basic characteristics of fluorine in SiO<sub>2</sub> gate oxide and on the Si / SiO<sub>2</sub> interface. On the one hand, the fluorine in gate oxide can substitute Si-H, Si-OH or Si-O strained bonds forming Si-F bonds which are not easy to break off due to its higher bonding energy<sup>[6]</sup>, resulting in the reduction of radiation-induced hole traps, and the stress relaxation of Si / SiO<sub>2</sub> interface correlated with interface hardness<sup>[1,15]</sup>. This is the positive effects of fluorine. On the other hand, the creation of too many lattice defects occurs such as non-bridging oxygen or E'centers caused by the reaction between fluorine and Si-O network<sup>[1]</sup>, and the defects induced by fluorine implantation is not immunized completely by post-implantation

annealing. This is the negative effects of fluorine. The proportion of positive and negative effects respond to the amount of  $F^+$  dose under identical other implantation conditions. For devices of lower  $F^+$  doses the negative effects are principal because the positive effects (with less amount of Si-F bonds) cannot compensate the negative effects (implantation damage and nonbridging oxygen). When excessive amounts of fluorine are incorporated, the negative effects are also dominant because of the saturation of the stress relaxation with increasing  $F^+$  doses<sup>[15]</sup> and more nonbridging oxygens. The beneficial effects exceed the negative effects for optimum fluorine concentration, resulting in more resistant to radiation damage than control devices. The difference of our optimum range with  $5 \times 10^{14} - 2 \times 10^{15} \text{cm}^{-2}$  reported by Y. Nishioka *et al.*<sup>[2]</sup> is attributed to  $F^+$  implantation conditions.

#### 4 SUMMARY

We have investigated systematically the radiation response dependences of fluorine implantation conditions, and found that the radiation responses in fluorinated oxides depend strongly on the layer, energy, annealing and amount of fluorine introduction. An optimum F implant range has been found to exist for a given technology, and in the case of this study, the optimum F range appears to  $5 \times 10^{14} - 2 \times 10^{16} \text{cm}^{-2}$ , particularly the optimum F dose being  $1 \times 10^{16} \text{cm}^{-2}$ . These results have been attributed to the formation of Si-F bonds, the interface stress relaxation and the less implantation defects.

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