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# **Performance Improvement of Aluminum doped MOHOS Total Dose Radiation Sensor Device by Fluorine Plasma Treatment**

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**Abstract:** Aluminum doped titanium nitride-silicon oxide-hafnium oxide-silicon oxide-silicon device with fluorine plasma treatment (hereafter F-Al-MOHOS) can be a candidate for total ionization dose (TID) radiation sensor application. In this report, the performance improvement in terms of TID radiation induced charge generation effect and charge-retention characterization for F-Al-MOHOS device is the main subject of this study. The F-Al-MOHOS reported in this study has demonstrated their potential application for non-volatile TID radiation in the future.

Keywords: high k; sensor; radiation; SONOS; SOHOS; MOS; TID

# 1. Introduction

Total ionizing dose (TID) radiation effect is the major application concern for the operation of electronic devices in advanced X-ray lithography semiconductor manufactory process and outer space application, as well as other harsh environments such as accelerators, where high and low energy particles exist. Total ionization dose (TID) radiation effects in traditional silicon-silicon dioxide-nitride-silicon dioxide-silicon (SONOS) non-volatile memory (NVM) devices have been studied previously. [1] Until now, little was known about the radiation response of SONOS–like devices with high k gate dielectric structure [2]. High-k gate dielectrics have been used for reducing transistor gate leakage current in the

advanced nano-scale CMOS device technology. [2] Recently, conventional SONOS flash memory is replaced with SOHOS memory device. However, SOHOS device has worse data retention characteristic as well known. [2] The effects of radiation response of a few hafnium-based MOS devices have been reported. [2–3] But the data retention reliability of hafnium-based SONOS–like device as TID radiation sensor has not been well studied and it will be the main subject of this study. In order to improve the data retention performance of hafnium-based SONOS–like device for TID radiation sensor application, an aluminum doped titanium nitride–silicon oxide–hafnium oxide–silicon oxide–silicon device with fluorine plasma treatment (hereafter F-Al-MOHOS) is fabricated. The electrical performance of F-Al-MOHOS with various doping treatment after radiation exposure including radiation induced charge generation effect and charge-retention characterization are the main subjects of discussion in this report.

#### 2. Experimental Section

F-Al-MOHOS devices with various doping treatment listed in Table 1, the N-channel MOHOS device were fabricated at the Taiwan National Nano Device Laboratories (NDL, Hsin-Chu, Taiwan). Starting wafers were 6" silicon (100) orientation with boron doped type substrates with a resistively of 15–25  $\Omega$ •cm. The tunneling silicon oxide SiO<sub>2</sub> was formed by using an advanced clustered vertical furnace on the wafers and its thickness was 3~5 nm, which was measured by spectroscopic ellipsometer. After the tunneling oxide formation, Si<sub>3</sub>N<sub>4</sub> (10~20 nm) was deposited as the chargetrapping layers by using low-pressure chemical vapor deposition (LPCVD) for N (MONOS) device and HfO<sub>2</sub> films (10~20 nm) were deposited as the charge-trapping layers for the H (MOHOS) device, with precursors Hf (tert-butoxy) 2 (mmp) 2 in a metal organic chemical vapor deposition (MOCVD) system at  $400 \sim 550^{\circ}$ C. Al doped HfO<sub>2</sub> films were deposited as the charge-trapping layers for A1 and A2 sample, using Hf (tert-butoxy)<sub>2</sub>(mmp)<sub>2</sub> and aluminum isopropoxide precursors in a metal organic chemical vapor deposition (MOCVD) system at 400 ~ 550 °C. A composition ratio between 20% and 30% of Al in Al doped MOHOS sample (hereafter Al-MOHOS) is achieved by controlling the deposition process parameters for A1 and A2 sample. To manipulate the F profile, CF<sub>4</sub> plasma with 30 sccm at 50W for 30 s condition was performed on (1) "F1" sample (CF<sub>4</sub> plasma before HfO<sub>2</sub> deposition) and on (2) "F2" sample (CF4 plasma after HfO2 deposition), and on (3) "AF" sample (CF4 plasma before and after HfO<sub>2</sub> deposition). However F1 sample and F2 sample, F treatment before HfO<sub>2</sub> deposition (hereafter pre F-MOHOS) and F treatment after HfO<sub>2</sub> deposition (hereafter post F-MOHOS), were prepared without Al doping. But AF sample, F treatment before and after HfO<sub>2</sub> deposition (hereafter pre-post F-MOHOS) was prepared with 20% Al doping. The blocking oxide (100–200 Å thickness) was deposited using LPCVD tetra ethyl oxysilane (TEOS) Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. The control gate with 200~400 nm TiN metal gate was formed by the DC sputtering for all samples. The resulting structure is illustrated the Figure 1a. After gate patterning, source and drain were formed by implantation with arsenic atoms which were activated at 900°C for 30s. For comparison purpose, all the devices listed in Table 1 are with the same thickness of tunneling oxide, trapping oxide and block oxide.

In this paper, the  $V_T$  shifts due to Gamma irradiation on the F-Al-MOHOS devices prepared with various doping treatment were measured. The Gamma irradiation was performed on the F-Al-MOHOS

devices with negative gate bias stress (NVS) ( $V_G = -5 V$ ) by using a <sup>60</sup>Co irradiator source at room temperature. The  $V_T$  change of F-Al-MOHOS devices with various doping treatment were examined after the Gamma irradiation. The  $V_T$  was measured at room temperature from the experimental results of I<sub>D</sub>-V<sub>G</sub> curves by using a HP4156A parameter analyzer. Figure 1b shows the charge generation and trapping states of the gate dielectric for the F-Al-MOHOS device under NVS after ionization radiation exposure.



**Figure 1.** F-Al-MOHOS device (**a**) schematic cross-section (**b**) charge generation and trapping during irradiation.

	Ν	Н	A1	A2	F1	F2	AF
Trapping layer	Si <sub>3</sub> N <sub>4</sub>	HfO <sub>2</sub>	HfO <sub>2</sub>	HfO <sub>2</sub>	HfO <sub>2</sub>	HfO <sub>2</sub>	HfO <sub>2</sub>
Al doping	no	no	20%	30%	no	no	20%
F treatment	no	no	no	no	Pre HfO <sub>2</sub> deposition	Post HfO <sub>2</sub> deposition	Pre and post HfO <sub>2</sub> deposition

Table 1. MOHOS devices prepared with various doping treatment in HfO<sub>2</sub> trapping layer.



Figure 2. (a)  $I_D$ -V<sub>G</sub> curve for MOHOS device after 5 Mrad TID gamma irradiation; (b) |dela V<sub>T</sub>| increase as a function of Gamma radiation TID for MOHOS device.



**Figure 3.** Comparison for F-Al-MOHOS devices with various doping treatment after 5 Mrad TID irradiation (a) for  $|Delta V_T|$  (b) for relative charge density.



**Figure 4.** Comparison for  $V_T$  change with 10yrs retention time under  $V_G = -5$  V for varies F-Al-MOHOS devices after (**a**) 10 krad TID irradiation (**b**) 5 Mrad TID irradiation.

## 3. Results and Discussion

Figure 2a shows I<sub>D</sub>-V<sub>G</sub> curve for a typical MOHOS device with NVS (V<sub>G</sub> = -5 V) and processed with Gamma radiation up to 5 Mrad TID. After 5Mrad irradiation, a significant negative V<sub>T</sub> shift of the MOHOS device is observed in the figure which is a result of increase of positive charges in the trapping layer caused by ionization radiation. The radiation-induced negative V<sub>T</sub> shift in the irradiated MOHOS device is induced by a combination of loss stored charge in the HfO<sub>2</sub> trapping layer and a build-up of positive charge from asymmetric trapping of electrons and holes in the trapping layer. [1,3] The |delta V<sub>T</sub>| of MOHOS device increases as a function of Gamma TID is indicated in Figure 2b. It also shows a quasi-linear correlation of |delta V<sub>T</sub>| versus Gamma TID below 100 krad in log scale, but |delta V<sub>T</sub>| increases more sharply after Gamma irradiation levels up to 100 krad TID. [1,3]

The  $|\text{delta V}_T|$  and charge density comparison after 5Mrad TID Gamma irradiation for various F-Al-MOHOS devices shown in Table 1 are illustrated in Figure 3a and Figure 3b, respectively. The trapped charge density can be calculated from delta V<sub>T</sub> using Terman method. [2] The radiation

induced V<sub>T</sub> shift of MOHOS without doping is more significant than that of SONOS, which results from more radiation induced trapped charges into the HfO<sub>2</sub> trapping layer than Si<sub>3</sub>N<sub>4</sub> charging layer. The improvement on the radiation induced V<sub>T</sub> shift effect can be achieved by tuning a suitable Al ratio in HfO<sub>2</sub> and the results indicate that more significant TID radiation induced charging effect is achieved with 20% Al content in the HfO<sub>2</sub> trapping layer in this study, as shown in Fig3a. Therefore, the improvements on the radiation induced V<sub>T</sub> shift performance in this paper may be attributed to the higher radiation induced positive trap density results from doping suitable Al content into the HfO<sub>2</sub> charge-trapping layer. In addition, radiation induced charge generation efficiency for MOHOS with F treatment sample (hereafter F-MOHOS) is also enhanced due to radiation induced high density positive trapped charges in F-MOHOS device due to fluorine incorporation into HfO<sub>2</sub> trapping layer. The experimental results show that radiation induced charge density of AF sample (F-Al-MOHOS device with 20% Al doping and F treatment both pre- and post-HfO<sub>2</sub> deposition) is 6 times larger than that of MONOS device.

In this section, V<sub>T</sub> retention time stability of MOHOS devices is discussed and these properties are important for their potential application usage for TID radiation sensor. It is noted that the decay of the V<sub>T</sub> with time for MOHOS device after irradiation is a result of charge tunneling out from the HfO<sub>2</sub> trapping layer. Figure 4a and Figure 4b shows the V<sub>T</sub> stability versus time under NVS ( $V_G = -5$  V) for F-Al-MOHOS devices with various implantation processes after 10Krad and 5Mrad TID Gamma irradiation, respectively. The device with HfO2 as the charge-storage layer shows the worst charge-retention characteristics compared to Si<sub>3</sub>N<sub>4</sub>. It seems that the device with HfO<sub>2</sub> trapping layer is degraded in term of data storage capacity by providing tunneling leakage path induced by HfO<sub>2</sub>-SiO<sub>2</sub> (O-H) interface trap states. [2] But the charge retention performance of Al-MOHOS can be increased by increasing the Al doping ratio up to 30%. Doping high percentage of Al into pure HfO<sub>2</sub> film can enhance the crystallization temperature of Al-HfO2 compound (Aluminum doped hafnium oxide) and improve the charge retention characteristic of the device due to improvement of leakage current after high temperature S/D annealing processes. [4] Meanwhile, the charge-retention characteristic of F plasma treatment MOHOS device has also been significantly improved. It shows that the charge-retention performance of the F-MOHOS device with NVS ( $V_G = -5 V$ ) after low TID (10 kard) irradiation, the condition of pre-F treatment is better than post-F treatment. But the charge-retention performance after high TID (5 Mard) irradiation for the F-MOHOS device with NVS ( $V_G = -5$  V), the condition of post-F treatment is better than pre-F treatment. This result obviously indicates that the pre-F-treatment is suggested to be used to improve V<sub>T</sub>-retention for low TID irradiated MOHOS device (with positive V<sub>T</sub> and in program state), the reason is that pre-F-treatment is viable for the passivation on the bottom tunneling path of charge storage layer (trapping oxide and tunneling oxide interface) in this case. Also, the post-F-treatment is recommended for the improvement of V<sub>T</sub>-retention for high TID irradiated MOHOS device (with negative V<sub>T</sub> and in erase state), because post-F-treatment is effective to passivate the top tunneling path of charge storage layer (trapping oxide and block oxide interface) in this device. [5]

#### 4. Conclusions

The experimental results show that radiation induced charge density of F-Al-MOHOS device with 20% Al doping and pre-post F treatment is 6 times larger than that of MONOS device. In brief, the significant improvements in terms of radiation induced charging effect and charge-retention characterization of F-Al-MOHOS device may be achieved by doping suitable Al content and pre-post F treatment for the HfO2 charge-trapping layer. The F-Al-MOHOS reported in this study has demonstrated their potential application for non-volatile TID radiation sensing application in the future.

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#### **Conflicts of Interest**

The authors declare no conflict of interest.

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