Performance Improvement of Total Ionization Dose Radiation Sensor Devices Using Fluorine-Treated MOHOS

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Abstract: Fluorine-treated titanium nitride–silicon oxide–hafnium oxide–silicon oxide–silicon devices (hereafter F-MOHOS) are candidates for total ionization dose (TID) radiation sensor applications. The main subject of the study reported herein is the performance improvement in terms of TID radiation-induced charge generation effect and charge-retention reliability characterization for F-MOHOS devices. In the case of F-MOHOS TID radiation sensors, the gamma radiation induces a significant decrease of threshold voltage $V_T$ and the radiation-induced charge density is nearly six times larger than that of standard metal–oxide–nitride–oxide–silicon MONOS devices. The decrease of $V_T$ for F-MOHOS after gamma irradiation has a strong correlation to the TID up to 5 Mrad gamma irradiation as well. The improvement of charge retention loss for F-MOHOS devices is nearly 15% better than that of metal–oxide–hafnium oxide–oxide–silicon MOHOS devices. The F-MOHOS device described in this study demonstrates better feasibility for non-volatile TID radiation sensing in the future.

Keywords: SONOS; NVM; sensor; gamma ray

1. Introduction

The total ionizing dose (TID) radiation-induced charging effect is a major application concern for the operation of electronic devices in advanced X-ray lithography semiconductor manufacturing processes and outer space applications. When a metal-silicon dioxide-silicon (MOS) structure is irradiated by gamma rays, positive charges build-up at the Si-SiO$_2$ interface and an interface state occurs in the structure [1]. The radiation-induced charging effects of a metal–nitride–oxide–silicon (MNOS) device with stacked insulation layers composed of silicon nitride and silicon dioxide have been reported [2]. The radiation-induced charging effects on traditional silicon–oxide–nitride–oxide–silicon (SONOS) nonvolatile memory (NVM) devices have also been studied before [3,4]. Until now, little was known about the radiation response of SONOS–like devices with high k charge-trapping structure [4,5]. High-k gate dielectrics have been used for reducing transistor gate leakage current in advanced nano-scale CMOS device technology [5]. Recently, conventional SONOS flash memory was replaced with silicon–oxide–hafnium oxide–oxide–silicon SOHOS devices (hafnium-based SONOS-like devices with high k material as charge-trapping structure). However, SOHOS devices have worse data retention characteristics, as is well known [5]. The effects of radiation response on a few SOHOS-like devices have been reported [4,5], but the charge retention reliability of the SOHOS 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 radiation-induced charge density and charge retention reliability of SOHOS device for non-volatile TID radiation sensor applications, a titanium nitride–silicon oxide–hafnium oxide–silicon oxide–silicon device with CF$_4$ plasma treated hafnium oxide HfO$_2$ (hereafter F-MOHOS) was fabricated. The electrical performance of F-MOHOS, including radiation-induced charge generation effect and charge retention reliability characterization, are the main subjects of discussion in this paper, which reports a study of different types of F-treated MOHOS to manipulate the radiation-induced charging effects and charge retention reliability characterization of F-treated HfO$_2$. In contrast to the previous publication [4], the MOHOS devices were irradiated by gamma irradiation with negative gate bias stress (NVS). The NVS application increases the survival yield of radiation-induced electron-hole pairs from the initial recombination process and also increases the radiation-induced charging yield of the MOS type devices [6].

2. Experimental Section

The MOHOS devices prepared with various F-treated HfO$_2$ materials are listed in Table 1. MOHOS structures were fabricated on p-type resistivity 15–25 $\Omega$-cm Si $<$100> substrate. To fabricate MONOS devices, we used thermal silicon oxide SiO$_2$ as tunneling oxide, CVD silicon nitride Si$_3$N$_4$ for the trapping layer, and CVD TEOS SiO$_2$ as blocking oxide. The tunneling oxide (SiO$_2$) was formed on the wafers by using an advanced clustered vertical furnace. After the tunneling oxide formation, silicon nitride (hereafter, nitride, Si$_3$N$_4$) was deposited as the charge-trapping layer by low-pressure chemical vapor deposition (LPCVD) for MONOS devices.

### Table 1. MOHOS devices prepared with various F treated HfO$_2$ as charge-trapping layer.

| Split | N | H | FB | FA | FAB |
|-------|---|---|----|----|-----|
| Charge-trapping layer | Si$_3$N$_4$ | HfO$_2$ | HfO$_2$ | HfO$_2$ | HfO$_2$ |
| F treatment | no | no | Before HfO$_2$ deposition | After HfO$_2$ deposition | before and after HfO$_2$ deposition |

For MOHOS devices, HfO$_2$ films (10–20 nm) were deposited as the charge-trapping layers, with H(fert-butoxy)$_2$(mmp)$_2$ precursor in a metal organic chemical vapor deposition (MOCVD) system at 400 $\sim$ 550 $^\circ$C. For F-MOHOS devices, CF$_4$ plasma treatment with 30 sccm at 50 W for 30 s was performed on MOHOS. To manipulate the radiation-induced charging effects in F-treated HfO$_2$, three type of F-treated MOHOS were prepared: (1) “FB” type MOHOS (hereafter FB-MOHOS), CF$_4$ plasma treatment before HfO$_2$ deposition; (2) “FA” type MOHOS (hereafter FA-MOHOS), CF$_4$ plasma treatment after HfO$_2$ deposition; (3) “FAB” type MOHOS (hereafter FAB-MOHOS), CF$_4$ plasma treatment both before and after HfO$_2$ deposition. The SiO$_2$–Si$_3$N$_4$–SiO$_2$ (hereafter ONO) gate stack consists of a 100 Å–200 Å silicon nitride and 50 Å–150 Å bottom and top silicon oxides. TiN metal gate (200–400 nm) was formed by DC sputtering for the control gate. After gate patterning, source and drain were formed by implantation with arsenic atoms which were activated at 900 $^\circ$C for 30 s. Figure 1a shows a cross-section view of the MOHOS devices. For comparison, all the devices listed in Table 1 have the same tunneling oxide, charge-trapping layer and blocking oxide layer thickness. A MOHOS device with dimensions W x L = 0.1 $\times$ 0.1 mm$^2$ was used in this paper.

For gamma TID data writing, in this study all the devices listed in Table 1 were exposed to $^{60}$Co gamma radiation with gate negative bias stress (NVS, $V_G = -4$ V). For the gamma TID data read, $V_T$ shifting was measured at room temperature using a HP4156A parameter analyzer. The of $I_D - V_G$ curve experimental results of the MOHOS device pre-irradiation and post-irradiation were compared by a computer-controlled HP4156A parameter analyzer at room temperature. Figure 1b shows the charge generation and trapping states of the gate dielectric in the FAB-MOHOS device after gamma irradiation.
This result is in agreement with those of previous studies [4].

The amount of decrease of charge density can be calculated by the Terman method [5]. As shown in Figure 3a, the radiation-induced irradiation for various F-MOHOS devices shown in Table 1 are illustrated in Figure 3a, b. The trapped delta $V_T$ of the MOHOS device increases as a function of gamma TID, as indicated in Figure 2a. The negative $V_T$ shift result agrees with those of previous studies [3, 4]. These radiation-induced shifts in the MOHOS device increases as a function of gamma TID, as indicated in Figure 2b. It also shows a quasi-linear correlation of $|\Delta V_T|$ increase as a function of gamma irradiation TID for MOHOS device.

3. Results and Discussion

3.1. Radiation-Induced Charging Effect of F-MOHOS after Gamma Irradiation

As illustrated in Figure 2a, the $I_D - V_G$ curve of MOHOS was shifted to the left after 5 Mrad TID of gamma irradiation. This implies that gamma irradiation induces a decrease of $V_T$ for MOHOS. The amount of decrease of $V_T$ is about 2.9 V. It is considered that the change is due to an increase in the net positive trapped charges in the HfO$_2$ charge-trapping layer after gamma irradiation. The negative $V_T$ shift result agrees with those of previous studies [3, 4]. These radiation-induced shifts in the irradiated device are a combination of two effects; the first effect is a result from the loss of stored negative charge in the HfO$_2$ trapping layer and the second effect is due to a build-up of positive charge resulted from asymmetric trapping of electrons and holes in the HfO$_2$ trapping layer.

The $|\Delta V_T|$ of the MOHOS device increases as a function of gamma TID, as indicated in Figure 2b. It also shows a quasi-linear correlation of $|\Delta V_T|$ vs. gamma TID below 100 krad in log scale, but $|\Delta V_T|$ increases more sharply after gamma irradiation at levels up to 100 krad TID. This result is in agreement with those of previous studies [4].

The radiation-induced $|\Delta V_T|$ and charge density comparisons after 5 Mrad TID gamma irradiation for various F-MOHOS devices shown in Table 1 are illustrated in Figure 3a, b. The trapped charge density can be calculated by the Terman method [5]. As shown in Figure 3a, the radiation-induced...
VT shift of MOHOS is more significant than that of MONOS, which results from more radiation-induced charges in the HfO2 trapping layer than in the Si3N4 charging layer. In addition, the F-MOHOS devices with various F treatments (FA-, FB- and FAB-MOHOS) all demonstrate higher degrees of VT shift and higher radiation-induced charge density than the MOHOS devices. These results are contributed by a higher radiation-induced charging effect on these F-MOHOS devices than that on MOHOS devices. Note that the radiation-induced charge density of the FAB-MOHOS device is six times larger than that of traditional MONOS devices. The FAB-MOHOS device with larger F-treatment volume in HfO2 has the higher radiation-induced charge density than the FA-MOHOS and FB-MOHOS devices after gamma irradiation.

Figure 3. (a) |ΔVT| for various F-MOHOS devices after 5 Mrad TID irradiation; (b) Relative charge density for various F-MOHOS devices after 5 Mrad TID irradiation.

3.2. VT Stability vs. Retention Time

In this section, the radiation-induced charges-retention reliability characteristics of the F-MOHOS devices are discussed and these are the important electrical properties that need to be verified for their potential application in TID radiation sensors in this study. The VT stability vs. time for MOHOS under VC = −4 V before gamma irradiation and after 5 Mrad gamma irradiation is illustrated in Figure 4a,b respectively.

Figure 4. The VT vs. retention time for MOHOS device: (a) before gamma irradiation; (b) after 5 Mrad gamma irradiation.

It is noted that the decrease of the VT with time for the pre-irradiated MOHOS device is a result of stored negative-charge tunneling out from the HfO2 trapping layer. Note that the increase of the
$V_T$ with time for the post-irradiated MOHOS device is a result of radiation-induced positive charges tunneling out from the HfO$_2$ trapping layer.

Figure 5a shows the $V_T$ stability versus time with NVS ($V_C = -4\ V$) for various F-MOHOS devices shown in Table 1 before gamma irradiation. It is seen that the device with HfO$_2$ as the charge-storage layer shows the worst charge retention reliability characteristics compared with Si$_3$N$_4$. The worse charge storage capacity in the MOHOS device may be attributed to tunneling leakage current induced by interface trap states [7]. As shown in Figure 5a, the F-MOHOS devices demonstrate better charge-retention reliability characteristics than MOHOS ones before gamma irradiation, which is because deep negative-charge traps in F treated trapping HfO$_2$ lead to less negative-charge loss and a better negative charge-retention reliability characteristics for the pre-irradiated F-MOHOS than the pre-irradiated MOHOS [7]. However, the FB-MOHOS device has better charge-retention reliability characteristics than the FA-MOHOS devices before gamma irradiation. Because the probability of stored negative-charge tunneling out from bottom of trapping HfO$_2$ to tunneling oxide is higher (compared to that from top of trapping HfO$_2$ to blocking oxide) for the pre-irradiated F-MOHOS device under NVS. Therefore, the FB-MOHOS device with deeper negative-charge traps at the bottom of HfO$_2$ shows better charge-retention reliability characteristic than the FA-MOHOS devices before gamma irradiation.

![Figure 5a](image1.png)

**Figure 5a.** The $V_T$ change with 10-years retention time for various F-MOHOS devices under $V_C = -4\ V$ after (a) 0 Mrad gamma irradiation; (b) 5 Mrad gamma irradiation.

Figure 5b shows the $V_T$ stability vs. time under $V_C = -4\ V$ for various F-MOHOS devices after 5 Mrad TID gamma irradiation. We note that the FA-MOHOS demonstrate worse charge-retention reliability characteristics than the FB-MOHOS after 5 Mrad gamma irradiation because the probability of radiation-induced positive charges tunnel-out from the top of trapping nitride to blocking oxide is higher (compared to that from bottom of trapping nitride to tunneling oxide) for the 5 Mrad gamma irradiated F-MOHOS device under NVS. Therefore, the FA-MOHOS device with more deep negative-charge traps at the top of HfO$_2$ shows better charge-retention reliability characteristic than the FB-MOHOS devices after 5 Mrad gamma irradiation. Furthermore, the F treatment process during HfO$_2$ deposition should be considered for the traded-off between pre-irradiated and post irradiated charge-retention reliability. Therefore, the FAB-MOHOS device with deeper negative-charge traps both at the top and bottom of HfO$_2$ is suggested for improvement of charge retention reliability characteristic both before gamma irradiation and after 5 Mrad gamma irradiation.

4. Conclusions

As shown by the experimental data, F treatment during HfO$_2$ deposition is a very effective process for enhancing the radiation-induced charging effect of MOHOS devices. It can be explained
by the fact that the enhanced radiation-induced charging effect of F-MOHOS was induced by more radiation-induced positive charges in the F-treated HfO$_2$ trapping layer. In addition, the F treatment process during HfO$_2$ deposition should be considered for the trade-off between pre-irradiated and post-irradiated charge-retention reliability. Therefore, the FAB-MOHOS device is suggested for improvement of charge retention reliability characteristics both before gamma irradiation and after 5 Mrad gamma irradiation. The results show that F-MOHOS devices with F-treated HfO$_2$ charge-trapping layers can be potential candidate nonvolatile TID radiation sensors in the future.

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**References**

1. McWhorter, P.J.; Miller, S.L.; Dellin, T.A. Radiation response of SNOS nonvolatile transistors. *IEEE Trans. Nucl. Sci.* **1986**, *NS-33*, 1414–1419. [CrossRef]

2. Draper, B.; Dockerty, R.; Shaneyfelt, M.; Habermehl, S.; Murray, J. Total dose radiation response of NROM-style SOI non-volatile memory elements. *IEEE Trans. Nucl. Sci.* **2008**, *55*, 3202–3205. [CrossRef]

3. Qiao, F.Y.; Yu, X.; Pan, L.Y. TID characterization of 0.13 μm SONOS cell in 4 Mb NOR Flash memory. In Proceedings of the 19th IEEE International Symposium on the Physical and Failure Analysis of Integrated Circuits (IPFA), Singapore, 2–6 July 2012.

4. Hsieh, W.C.; Lee, H.T.; Jong, F.C. An Ionizing Radiation Sensor Using a Pre-Programmed MAHAOS Device. *Sensors* **2014**, *14*, 14553–14566. [CrossRef] [PubMed]

5. Cheng, Y.H.; Ding, M.; Wu, X.L.; Xin, L.; Wu, K. Irradiation Effect of HfO$_2$ MOS Structure under Gamma-ray. In Proceedings of the IEEE International Conference on Solid Dielectrics, Bologna, Italy, 30 June–4 July 2013.

6. Oldham, T.R.; McLean, F.B. Total Ionizing Dose Effects in MOS Oxides and Devices. *IEEE Trans. Nucl. Sci.* **2003**, *50*, 483–499. [CrossRef]

7. Wu, W.C.; Lai, C.S.; Wang, T.M.; Wang, J.C.; Hsu, C.W.; Ma, M.W.; Lo, W.C.; Chao, T.S. Carrier Transportation Mechanism of the TaN/HfO$_2$/IL/Si Structure With Silicon Surface Fluorine Implantation. *IEEE Trans. Electron. Devices* **2008**, *55*, 1639–1646. [CrossRef]

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