A Promising Method to Improve the Bias-Stress and Biased-Radiation-Stress Stabilities of Solution-Processed AlOx Thin Films

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The effects of hydrogen peroxide (H2O2) on the device properties and stabilities of solution-processed AlOx metal-oxide-semiconductor capacitors (MOSCAPs) were investigated. It is demonstrated that H2O2 is a strong oxidizer to decompose precursor residuals, reduce oxygen vacancy (Vo) and defects density of solution-processed AlOx thin films. The interface quality and the bias-stress (BS) stability of AlOx MOSCAPs were improved by employing H2O2. Furthermore, through carrying out on-site measurements, 7.5 M H2O2 AlOx MOSCAPs exhibited ignorable radiation-induced oxide traps and interface traps under biased-radiation-stress (BRS) with a total dose up to 42 Gy (SiO2). The 7.5 M H2O2 AlOx MOSCAPs also demonstrate the ability to recover under radiation after the bias was interrupted. The reduced number of Vo and high AlOx concentration of 7.5 M H2O2 AlOx could suppress the radiation-induced trapping/de-trapping behavior among the AlOx bulk and the breaking of Si-H bonds at the AlOx/Si interface. Besides, through biased-illumination-stress (BIS) measurements, the breaking of Si-H bonds under negative biased-radiation-stress (NBRS) was further proved. The results demonstrate that employing H2O2 in the solution-process is simple and effective; it has significant potential to improve the stabilities of large-area electronics for nuclear and aerospace applications.

***Keywords***—***Solution-process, H2O2, High-k gate dielectric, AlOx capacitor, Gamma irradiation, On-site radiation measurements.***

# Introduction

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ver the past decade, solution-processed thin film deposition techniques for oxide materials have been well developed, including dip-coating [1, 2], spin-coating [3-6], and inkjet-printing [7, 8]. Compared to traditional vacuum thin film deposition methods, solution-processes enable the fabrication of larger area flexible devices due to the advantages of simplicity, low cost, and high throughput. Furthermore, solution-processed high-*k* oxide dielectrics enable the low leakage current, low operation voltage, and ease process integration with solution-processed devices [9-11]. However, solution-processing brings poor film quality and stability. Improving the reliability of solution-processed dielectrics becomes challenging, especially those devices for nuclear and aerospace applications. It is reported that solution-processed AlOx thin films suffer from inferior bias-stress (BS) and biased-radiation-stress (BRS) stabilities compared to those fabricated by traditional vacuum methods, which severely limits their practical applications [12-14]. Some literature has improved the BS stability of solution-processed devices through high-pressure annealing [15], doping with carrier suppressor [16, 17], UV treatment [18] and diffusion between different materials [19]. In these works, the BS stability of solution-processed devices has been examined and discussed together with the mechanism in detail. However, a few studies have been conducted on the stability of solution-processed devices under BRS [12, 14, 20, 21]. As solution-process is crucial to large-area electronics in harsh radiation environments, such as whole-body-scanning X-ray detectors and large-area antenna arrays [20]. Furthermore, the methods to improve the BRS stability of solution-processed devices have been seldomly reported and need to be explored [20]. [[1]](#footnote-1)

Hydrogen peroxide (H2O2) is a suitable oxidizer for solution-processing to improve the thin film quality and stability; it is environmentally friendly since it decomposes to give only water and oxygen as the reaction products, which makes it one of the cleanest, most versatile chemical oxidants available [22]. Through strong oxidation, H2O2 could decompose the chemicals and impurities at low temperature and combine with oxygen-related defects within oxide layers, which helps to reduce the oxygen vacancy (Vo) density in AlOx bulk and interface traps density at dielectric/semiconductor interface [23]. Comparing to other methods reported to improve the thin film quality and stability[15-19], utilizing H2O2 in the solution-process is simple, effective, and low-cost. Besides, the reduced number of Vo and high metal oxide concentration brought by H2O2 could suppress the radiation-induced trapping/de-trapping behaviors among the AlOx bulk and the breaking of Si-H bonds at the dielectric/semiconductor interface, thus improve the radiation hardness of the thin film.

The applied voltage bias-stress on devices will enhance the motion, reaction, and trapping of charges at or near the oxide/semiconductor interface [24]. Therefore, the long-term reliability of solution-processed devices under BRS needs to be investigated. For the conventional off-site radiation response method, the electrical characteristics of devices were evaluated before and after irradiation. The interruption of irradiation can cause a rapid recovery of the flat band voltage (VFB) shift, leading to underestimating the degradation caused by radiation-induced charge trapping/de-trapping. Consequently, on-site measurements have been introduced to fully characterize radiation-induced degradation. There has been limited research reported on the γ-ray radiation response of solution-processed high*-k* dielectrics by on-site techniques [25].

In this work, H2O2 was employed to improve the quality and stability of solution-processed AlOx thin films. AlOx thin films with high quality, low oxide trap, and semiconductor/oxide interface trap density were successfully fabricated at low temperature (~260 oC). The BS and BRS stabilities of aqueous solution-processed AlOx MOSCAPs with 7.5 M H2O2 were investigated with stress time up to 46000 s and total dose up to 42 Gy (SiO2) by an on-site technique. In addition, the radiation-induced oxide trap variation, interface trap variation and the recovery behavior of AlOx MOSCAPs were preciously analyzed.

# Experimental Details

The fabrication process of H2O2 AlOx is shown in Fig. S1 in the supporting information. 0.6 M (Al(NO3)3·xH2O) was dissolved in de-ionized (DI) water with 0-10 M H2O2, and the solution was stirred for 6 h and filtered by a 0.22 µm Polytetrafluoroethylene (PTFE) syringe filter before spin coating. To prepare the substrates, single-crystal lightly doped N-type silicon wafers (orientation: 100, doping concentration: ~1015 cm-3, resistivity: 2-4 Ω·cm) were dipped in 2 % HF aqueous solution for 30 s to remove the native oxide and then dried by N2. Subsequently, the Si substrates were exposed under air plasma for 30 mins to increase their hydrophilia. Then the precursor solution was spin-coated on the processed substrate at 4000 rpm for 40 s. Then the samples were directly transferred to a hot plate set to 125 °C and ramped to a final annealing temperature of 260 oC at a rate of 25 oC min-1 and held for 1 h. Finally, 300 nm thick Al top and bottom electrodes were deposited through shadow masks by e-beam evaporation. The circular top electrode had a diameter of 0.3 mm.

The thickness of the solution-processed AlOx thin films was measured by spectroscopic ellipsometry. To investigate the thermal behavior of the precursor powder, the precursor solution was dried at 100 oC for 1 h and then monitored by thermogravimetric analysis-differential scanning calorimetry (TGA-DSC). The metal-oxide (M-O) lattice formation and impurity contents of AlOx thin films were characterized by X-ray photoelectron spectroscopy (XPS). The capacitance-voltage (C-V) characteristics were measured using a HP 4284 precision LCR meter at a frequency of 1 MHz. To investigate the BS and BRS stability of AlOx MOSCAPs, constant voltage bias stress was applied on the gate with and without radiation exposure. During the bias-stress, C-V curves were measured at regular points in time of 101/3 s, 102/3 s, 103/3 s, 104/3 s, 105/3 s etc. to allow extraction of the VFB. For BRS, a 662-keV Cs137 γ-ray radiation source was used, the stress time was up to 46000s and the total dose was up to 42 Gy (SiO2). The dose rate is ~ 0.9 mGy/s. All electrical measurements were carried out in the dark at room temperature.

# Results and discussion

## Pre-radiation results

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| Table I Summarized Thin Film and Device Properties of AlOx Metal-Oxide-Semiconductor Capacitor (MOSCAP).

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| **H2O2 concentration****(M)** | **Thickness****(nm)** | **Leakage Current at** **4 V (10-5A/cm2)** | **Areal Capacitance (nF/cm2) at 1 kHz** | **Dielectric Constant at** **1 kHz** |
| 0 | 25.3 | 3.00 | 207 | 6.29 |
| 2.5 | 24.7 | 1.24 | 215 | 6.42 |
| 5.0 | 23.2 | 1.11 | 234 | 6.56 |
| 7.5 | 22.5 | 0.32 | 248 | 6.72 |
| 10 | 21.5 | 0.61 | 237 | 6.23 |

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| Fig. 1. (a) Capacitance-voltage (C-V), (b) the calculated interface trap density (Dit) in the Ec-Et range of 0.37 eV to 0.51 eV of AlOx MOSCAPs with different H2O2 concentration (0 M, 2.5 M, 5.0 M, 7.5 M, 10 M). |

Table I summarizes the properties of H2O2 AlOx thin films and MOSCAPs with different H2O2 concentration. The C-V curves measured at 1 MHz of AlOx MOSCAPs are displayed in Fig. 1a; at least 5 devices of each H2O2 concentration were measured, as shown in Fig. S2. It is found that the C-V curves of 7.5 M H2O2 MOSCAPs had larger Cmax, larger slope in the depletion region than other devices. The large Cmax corresponding to higher AlOx metal oxide framework concentration and the large slope of the C-V curves in the depletion region represents the enhanced interface quality with fewer interface traps.

To determine the effect of H2O2 in reducing interface trap density of AlOx MOSCAPs, C-V curves were carried out under measurement frequency (*f*m) from 1 kHz-1 MHz. Because higher *f*m can only detect shallower interface states with higher characteristic interface trap frequency (*f*it); thus, a higher gate voltage (VG) is required to pull down the conduction band at the interface. It is reported that the capture cross-section of the interface traps varies from 1.4×10-15 cm2 to 1.4×10-14 cm2 when the traps energy level located from Ec-Et = 0.24 eV to 0.73 eV. In order to avoid underestimating the interface trap density, it is assumed that the electron capture cross section at the interface $σ\_{n} $was1×10-14 cm2 in this work, which gives the value of Dit in the energy level range from 0.37 eV to 0.51 eV from the conduction band edge. Fig. 1b displays the comparison of Dit at

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| Fig. 2. (a) Leakage behavior (Jleak-V) and (b) positive & negative bias-stress (BS) stability of AlOx MOSCAPs with different H2O2 concentration (0 M, 2.5 M, 5.0 M, 7.5 M, 10 M). |

Ec-Et=0.37 eV, with H2O2 concentration increasing from 0 M to 7.5 M, the Dit reduced from 6.35×1012 cm-2eV-1 to3.72×1012 cm-2eV-1, the results are comparable to the value (2.2×1013 cm-2eV-1) calculated from high-*k* oxide MOSCAPs reported in [26]. However, as the H2O2 concentration increased to around 10 M, there is an increase of Dit from 3.72×1012 cm-2eV-1(7.5 M) to 5.72×1012 cm-2eV-1 (10 M). This phenomenon could be probably ascribed to the quick condensation of precursor accompanied with O2 releasing. The strong oxidation of H2O2 could lead to a rough semiconductor/oxide interface with increasing interface trap density [27].

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| Fig. 3. TGA curves of Al(NO3)3 precursor powder **(a)** with 0 M H2O2 and **(b)** with 7.5 M H2O2 heated from 20 to 500 oC with a heating rate of 10 oC/min. |

Leakage behavior (Jleak-Vg) of the AlOx thin films was investigated and shown in Fig. 2a. It can be observed that adding H2O2 reduced Jleak effectively, which is attributed to the improved film quality with reduced structure defects, precursor impurities, and Vo. In this situation, the leakage paths were suppressed, and the leakage current was reduced accordingly. As shown in Fig. S3, the ln(J/E) versus E1/2 is linear, indicating the mechanism of the leakage current may be the Poole-Frenkel (PF) emission since it is usually assigned as the dominating leakage mechanism in metal-insulator-metal thin film stacks [28].

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| Fig. 4. X-ray photoelectron spectroscopy (XPS) spectra ofO 1s narrow scans of solution-processed AlOx films. |

The BS stability of AlOx MOSCAPs were investigated under gate voltage stress (VGS\_Stress) = + 2 V and VGS\_Stress= - 2 V with stress time up to 1000 s. The extracted flat-band voltage shift (ΔVFB)is demonstrated in Fig. 2b. As the H2O2 concentration increased, the BS stability is gradually improved, and 7.5 M AlOx MOSCAP have the best BS stability, corresponding to its best thin film quality with reduced Vo and defects.

## Mechanism of employing H2O2

TGA-DSC curves of AlOx precursor powder are shown in Fig. 3a and b. AlOx thin films with 0 M and 7.5 M H2O2 concentration were selected for comparison, as AlOx MOCAPs with 7.5 M H2O2 concentration have demonstrated the best device properties and BS stability. The formation of the thin film can be divided into three stages. The first stage was the decomposition of the precursor. At this stage, most of the chemicals were vaporized, precursors were decomposed, and then hydrolyzed metals (M-OH, M, metal; O, oxygen; and H, hydrogen) were formed. The second stage was called the formation of the film. This stage began with a large exothermic reaction peak, as seen in the red lines in Fig. 3. M-OH were converted to metal oxide (M-O) gradually to form film during this stage. The third stage followed the exothermic reaction peak and was called the densification of film. It can be found in Fig. 3b that the exothermic reaction peak of precursor powder with 7.5 M H2O2 occurs at 120 oC, which was lower than the temperature (180 oC) of precursor powder with 0 M H2O2 in Fig. 3a. This indicated the decomposition of impurities was accelerated, which could start at lower temperature: huge molecules broke down into tiny volatile molecules, such as oxygen and water, during the strong oxidizing reaction of H2O2 [29]. During this process, H2O2 was decomposed by pyrolysis, and hydroxyl radicals (OH•) were released through the stepwise reactions below.

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|  | $$H\_{2}O\_{2}\rightarrow 2OH$$ | (1) |
|  | $$OH+H\_{2}O\_{2}\rightarrow HO\_{2}+H\_{2}O$$ | (2) |
|  | $$OH+HO\_{2}\rightarrow H\_{2}O+O\_{2}$$ | (3) |

All reaction equations are based on related papers [22, 27]. Although hydroxyl radicals lived a very short time during reactions, they acted as a powerful oxidizer and could accelerate the decomposition of solvent residues because of a higher oxidation potential than H2O2 [30]. Besides, the precursor powder 7.5 M H2O2 had around 30 % weight left at 300 oC, which was less than that (40 %) of precursor powder with 0 M H2O2, indicating more impurities were vaporized and decomposed during the annealing process. Consequently, adding 7.5M H2O2 could form dense films with an increased percentage of AlOx metal oxide and reduced defect sites at the specified annealing temperature.

In order to further explore the effects of employing H2O2 on the M-O lattice formation and impurity contents of AlOx thin films, XPS spectra are performed in Fig. 4.By applying Gaussian-Lorenz fitting method, the O1s peaks were deconvoluted into two peaks represent low bind energy (OI, 530.9 eV) and high binding energy (OII, 532.3 eV). The peak of OI is connected to O2- ions combined with Al ions, and the peak of OII is assigned to bonded oxygen, such as oxygen vacancy, hydroxyl groups, or absorbed H2O on the film surface [22, 27]. The fraction of [OI/ (OI + OII)] increased from 56.4 % to 68.1 % after adding 7.5 M H2O2, whereas the ratio of [OII/ (OI + OII)] decreased from 43.6% to 31.9 %. The strong oxidizing reactions of H2O2 could form a metal oxide framework at a low temperature and suppress the number of oxygen vacancies as well as other defects. The increased AlOx metal oxide concentration, reduced oxygen vacancies and M-OH content could diminish the trap state density, which improved the stability of integrated MOS devices accordingly.

## Biased-radiation-stress (BRS) stability

To investigate the BRS stability of 7.5 M H2O2 AlOx and 0 M H2O2 AlOx capacitors, the device degradation caused by radiation-exposure-only needs to be determined first. Consequently, ΔVFB under No-Bias and radiation-exposure-only was calculated and summarized in Fig. 5 (a)-(c). It is observed that the radiation could barely affect the ΔVFB of 7.5 M H2O2 AlOx capacitors, whereas the 0 M H2O2 AlOx capacitors suffered from the radiation caused degradation under radiation-exposure-only. Radiation could generate electron-hole pairs (EHPs) when passing through oxide [31]. It is reported that the EHPs would have no significant effect on devices without an applied electric field [32]. Therefore, the device response under PBRS and NBRS should be the focus when investigating the radiation hardness of a device.

To investigate the improved BRS stability of 7.5M H2O2 AlOx thin films compared to 0 M H2O2 AlOx thin films, voltage bias was applied on the gate of devices during radiation exposure, and the radiation exposure was not interrupted when carrying out the C-V measurement during the BRS investigation. In order to separate the BRS effect and BS effect, the BS results are provided for comparison, as shown in Fig. 5 (d)–(i). Under NBRS, the stress time was 46000 s, and the total dose was up to 42 Gy (SiO2). However, under PBRS, the stress time was only 100 s, and the total dose was up to 0.1 Gy. The reason is that the devices exhibited severe property degradation under PBS corresponded to a large ΔVFB, and the stress time was shortened accordingly. It can be found in Fig. 5d and g that BRS could barely lead to an additional ΔVFB in the 7.5 M H2O2 AlOx device compared to BS. However, 0 M H2O2 AlOx exhibited BRS induced device degradation corresponding to a more significant C-V shift.

The ΔVFB of AlOx MOSCAPs under PBS and PBRS are shown in Fig. 5d, and the distributions of ΔVFB under PBRS are shown in Fig. S5a. The time dependence of ΔVFB under BS and BRS is in agreement with the stretched exponential equation, which can be expressed as [33]:

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|  | $$∆V\_{FB}=∆V\_{FB0}(1-exp⁡(-\left(\frac{t}{τ}\right)^{β})$$ | (4) |

where ΔVFB0 is the ΔVFB at infinite time, $τ$ is the characteristic trapping time of carriers, and $β$ is the stretched exponential exponent. The stretched-exponential time dependence model hypothesized the emission of trapped charges toward deep states in the bulk dielectric for a long stress time (t >$ τ$) and large stress field. It is plausible that the amorphous structure of the gate dielectric will lend itself to an appreciable number of band-tail states which can act as transport states for the emitted lower energy trapped state charge [34], but the extent can be different depending on the materials or deposition condition of

dielectric layers. The fitted values are listed in Table S1 and Table S2; the results are consistent with those from the literature [34, 35], where the value of ΔVFB0 is mainly determined by the bias stress amplitudes and interface qualities. 7.5 M H2O2 devices have larger $τ$ than 0 M H2O2 devices, indicating the slower degradation under BS and BRS measurements.

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| Fig. 5. (a) ΔVFB and stretched exponential fitting results,(b) ΔNot and (c) ΔNit of AlOx MOSCAPs under positive bias-stress (PBS) and positive biased-radiation-stress (PBRS). (d) ΔVFB and stretched exponential fitting results,(e) ΔNot and (f) ΔNit of AlOx MOSCAPs under negative bias-stress (NBS) and negative biased-radiation-stress (NBRS). |

ΔVFB is the combined effect of ΔNot in AlOx bulk and ΔNit at the AlOx/Si interface. ΔNot causes the parallel shift of C-V curves, while ΔNit influences the stretch-out of C-V curves. ΔNot can be estimated by equation (5) [36]:

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|  | $$ΔN\_{ot}=-\frac{C\_{ox}∆V\_{mg}}{qA}$$ | (5) |

where ΔVmg is the mid-gap voltage shift obtained from C-V curves, Cox is the gate capacitance, qis the electronic charge and A is the electrode area. ΔNit was estimated by equation(6) [36]:

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|  | $$∆N\_{it}=\frac{C\_{ox}(∆V\_{FB}-∆V\_{mg})}{qA}$$ | (6) |

Fig. 5eand f show ΔNot and ΔNit of 7.5 M H2O2 AlOx, respectively. No radiation-induced oxide traps or interface traps were observed under PBRS, whereas PBRS could cause a reduced positive ΔVFB of 0 M H2O2 AlOx, corresponding to radiation-induced electron trapping in AlOx bulk. The generation of radiation-induced interface traps was negligible for all devices. The reason is that the generation of radiation-induced interface traps is related to the transport of radiation-induced holes and H+. Interface trap buildup occurs on time frames much slower than oxide-trap charge buildup; it takes place over many decades in time [37]. As a result, the PBRS time (100 s) was too short to affect interface trap density significantly.

As analyzed during the PBRS part, for 0 M H2O2 AlOx, radiation could form negative oxide traps under PBRS, which was probably ascribed to the radiation-induced electron trapping in AlOx bulk. This trapping behavior is highly sensitive to the electric field across the oxide during the radiation exposure, and switching the polarity of the bias-stress voltage should prevent the radiation-induced electron trapping. As a result, the device degradation under NBRS was then investigated. ΔVFB under NBS and NBRS is demonstrated in Fig. 5g, the distribution of and ΔVFB under NBRS is shown in Fig. S5b. For 7.5 M H2O2 AlOx, NBRS could not cause additional positive ΔVFB compared to NBS, indicating electron trapping in AlOx bulk dominate the device property degradation under PBRS, and this trapping behavior was suppressed under NBRS in a short time. However, as the NBRS time increased, it resulted in a negative ΔVFB of 0 M H2O2 AlOx, indicating that switching bias suppressed the radiation-induced electron trapping and led to radiation-induced positive charges. ΔNot and ΔNit of AlOx MOSCAPs under NBRS were shown in Fig. 5h andi, respectively. No significant radiation-induced oxide traps or interface traps can be found in 7.5 M H2O2 AlOx, whereas positive oxide traps and negative interface traps were generated under NBRS in 0 M H2O2 AlOx. This could be ascribed to the breaking of Si-H bonds and AlOx/Si interface, which contributes to an oxide trap (H+) and an interface trap (Si-) under NBRS; the detailed mechanism will be discussed with the assistance of energy band diagram later.

TGA and XPS results indicate that adding H2O2 in the solution-process could transfer M-OH into the M-O framework at low temperature and result in higher AlOx metal oxide concentration in 7.5 M H2O2 AlOx thin films than in 0 M H2O2 AlOx thin films. In addition, H2O2 also suppressed the oxygen vacancy density, removed the precursor impurities, and enhanced the AlOx/Si interface through its strong oxidation. The J-V and C-V results further prove the improvement of employing H2O2. As a result, the BS and BRS stabilities of the devices were improved by adding H2O2.

## Mechanism of BRS induced degradation

According to the characterization results, the energy band diagrams of solution-processed AlOx MOSCAPs under PBRS and NBRS can be displayed in Fig. 6a and b, respectively. For 0 M H2O2 AlOx capacitors, reduced positive ΔNot was observed under PBRS compared to PBS. The decreased positive ΔNot was probably ascribed to radiation-induced electron trapping (process (3) in Fig. 6a). Radiation exposure and electric bias could form neutral traps among the AlOx bulk near the AlOx/Si interface [38]. Meanwhile, electrons in the Si substrate accumulated near the AlOx/Si interface under a positive applied electric field. After that, those accumulated electrons could tunnel into the radiation generated traps and form negatively charged oxide traps, resulting in a reduced positive ΔNot [39, 40]. Besides, it is reported that Vo in oxide could significantly

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| Fig. 6. Energy band diagrams of solution-processed AlOx MOSCAPs under **(a)** PBRS and **(b)** NBRS. |

degrade the device hardness by acting as trapping sites [41]. According to the XPS results and leakage behavior, 0 M H2O2 AlOx capacitors exhibited higher defect density and larger leakage current than 7.5 M H2O2 AlOx capacitors, which further verified that radiation-induced electron trapping dominated the generation of negative ΔNot observed in Fig. 5b.

Unlike oxide traps, radiation had a negligible effect on the interface trap density under PBRS. The interface-trap buildup is a two-stage process [37, 42]. During the first stage, EHPs are generated in AlOx under radiation exposure (process (1) in Fig. 6a). With a positive applied electrical field, the electrons are sweep out of AlOx thin film in picoseconds, whereas the holes are transported through AlOx and trapped near the AlOx/Si interface to form an oxide trap. The transportation is accompanied by the release of hydrogen, in the form of H+ (process (2) in Fig. 6b). In the second stage, the released H+ move towards the AlOx/Si interface and passivate the Si- (reaction (7)). Once a defect is passivated by hydrogen, it no longer functions as an interface trap.

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|  | $$Si^{-}+H^{+}\rightarrow Si-H$$ | (7) |

The generation of radiation-induced interface traps is negligible for all devices. The PBRS time was too short (100 s) to generate significant radiation-induced interface traps.

7.5 M H2O2 AlOx capacitors have demonstrated improved radiation hardness under PBRS with ignorable radiation-induced ΔNot and ΔNit compared to 0 M H2O2 AlOx capacitors, which is likely due to the dense film with low defect density (Vo) and leakage current. The reduced number of Vo and high AlOx concentration could suppress the radiation-induced

electron trapping behavior. Thereby, the radiation hardness of AlOx devices under PBRS was improved by employing H2O2.

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| Fig. 7. ΔVFB recovery characteristics of solution-processed AlOx MOSCAPs after (a) PBS & PBRS and (b) NBS & NBRS. |

Under NBRS, for 0 M H2O2 AlOx devices, negative ΔNot was decreased in magnitude, whereas negative ΔNit was produced. As shown in Fig. 6b, under negative applied gate voltage, the radiation-induced electron tunnelling from substrate and trapping among AlOx bulk were suppressed. Instead, the breaking of Si-H bonds at the AlOx/Si interface dominated the device radiation response, which could contribute to an interface trap (Si-) and an available H+ that can be trapped in AlOx to serve as an oxide trap (reaction (8)) [24].

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|  | $$Si-H\rightarrow Si^{-}+H^{+}$$ | (8) |

Density-functional-theory calculations have demonstrated that the simple thermally assisted Si-H bond breaking is highly improbable for a passivated interface dangling bond under normal device operating conditions, such as simply voltage bias-stress at room temperature [43]. However, the applied electric field combined with radiation exposure can reduce the binding energy of a Si-H bond. Some candidates can facilitate breaking Si-H bonds, including the impurity Al atoms and suboxide bonds near the AlOx/Si interface [44]. It has been proved that 0 M H2O2 AlOx thin films contain a high concentration of metal hydroxide and a large density of oxygen vacancy. As a result, as the NBRS time increased, the breaking of Si-H bonds at the AlOx/Si interface leads to the variations of ΔNot and ΔNit.

On the other hand, 7.5 M H2O2 AlOx capacitors had satisfied radiation hardness under NBRS; no additional radiation-induced ΔNot or ΔNit could be found. The previous characterization results reveal that 7.5 M H2O2 AlOx thin film contained enhanced metal-oxygen lattice, reduced Vo, and hydroxide species, indicating the amount of impurity Al atoms and suboxide bonds were reduced. The first-principle Hartree-Fock calculation [45] shows that the hydrogen bonding energy increases when the Si–O–Si angle reduces. With an improved oxide/semiconductor interface, the Si–O–Si bond can be less stretched, which leads to a stronger hydrogen bond. Similarly, for thinner and denser AlOx thin films, the breaking of Si-H bonds could be suppressed. Besides, the improved film quality with reduced defect density limited the radiation-induced trapping/de-trapping behaviors in 7.5 M H2O2 AlOx devices. Consequently, the radiation hardness of 7.5 M H2O2 AlOx capacitors under NBRS was improved accordingly.

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| Fig. 8. Percent fading values of solution-processed AlOx MOSCAPs after different (a) BS and (b) BRS conditions. |

To further verify the radiation-induced damage under NBRS, the negative biased-illumination-stress (NBIS) was performed. The photon emitted by the LED has very low photon energy (~2.73 eV with λ ≈ 455 nm) compared to the energy (662 keV) of the photon emitted by the photon Cs137 γ-ray radiation source used in this work. The Si-H bonds at the Si/AlOx interface should not be broke by the incident light and lead to positive oxide traps. ΔVFB and the distribution of ΔVFB measured from at least 3 devices under NBS and NBIS are demonstrated in Fig. S6. As expected, both 7.5 M H2O2 AlOx and 0 M H2O2 AlOx exhibited NBIS induced positive VFB shift.

## Fading characteristics

As the voltage bias during the radiation exposure facilitated the motion of radiation-induced EHPs and thus degraded the device properties severely. The recovery behavior of the device under radiation exposure after the bias-stress was removed is a crucial issue to be investigated. Fig. 7 display the recovery behavior of the devices under BS and BRS, respectively. The BS and BRS induced degradation involved two components, a permanent (fixed) component, which was not decreased after stress removal, and a reversible component, which followed the applied stress bias dynamically. The devices recovered quickly when the bias-stress voltage was interrupted, demonstrating a self-healing ability. However, compared to the recovery behavior under BS, BRS still induced permanent damage to all devices. The device's recovery was related to the annealing of radiation-induced oxide traps, which was probably ascribed to that interface traps annealing requires high temperature [46]. The decreased fading values suggested that BRS induced oxide traps cannot be annealed and lead to permanent damage to AlOx thin films. Generally, the neutralization of oxide trapped charge occurs primarily by one of two mechanisms: 1) the tunnelling of electrons from the silicon into either oxide traps [47] or electron traps associated with trapped holes [48], and/or 2) the thermal emission of electrons from the oxide valence band into oxide traps [49].

To better estimate the spontaneous recovery behavior of the MOSCAPs at room temperature, the fading characteristic is essential [50]. The percent fading value can be calculated from [51]:

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|  | $$f=\frac{V\_{FB}(0)-V\_{FB}(t)}{V\_{FB}(0)-V\_{FB}}×100\%$$ | (9) |

where VFB is the fresh flat band voltage, VFB(0) is the flat band voltage immediately after bias stress experiment, and VFB(t) is the flat band voltage after annealing time t. The fading values of 7.5 M H2O2 AlOx and 0 M H2O2 AlOx MOSCAPs after BS and BRS are shown in Fig. 8. It can be found that fading values were decreased under BRS compared to BS, except for the 0 M H2O2 AlOx device under NBRS; it even increased after NBRS. Nevertheless, 7.5 M H2O2 devices exhibit higher fading values than 0 M H2O2 devices, indicating improved spontaneous recovery ability.

# Conclusion

The method to improve the BS and BRS stabilities of solution-processed AlOx was explored. H2O2 was employed in the precursor solution as a strong oxidizer. In addition, H2O2 suppressed the oxygen vacancy density, removed the precursor impurities, and enhanced the AlOx/Si interface through its strong oxidation at low temperature. The J-V and C-V results further proved the enhancement of employing H2O2. In addition, the reliability of the devices was improved by adding H2O2. 7.5 M H2O2 AlOx devices had demonstrated enhanced BS and BRS stabilities with stress time up to 46000 s and total dose up to 42 Gy (SiO2). When the devices were under BRS, H2O2 could suppress the transportation and reaction of hydrogen (e.g., breaking of Si-H bond), the electron trapping into radiation generated neutral traps and the Vo among AlOx bulk. ΔNit was insignificant compared to ΔNot, which was ascribed to that interface trap buildup occurs on time frames much slower than the oxide-trap charge buildup. The degradation involved a permanent (fixed) component and a reversible component. It is found that BRS could result in permanent damage to all devices; 7.5 M H2O2AlOx devices exhibited stronger recoverability than those with 0 M H2O2. The results in this work indicated that employing H2O2 in the solution-process had significant potential to improve the BS and BRS stabilities of large-area electronics applied for the nuclear environment and display area.

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