1. High-performance and radiation-hardened solution-processed ZrLaO gate dielectrics for large area applications

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## Abstract

Radiation hardness is important for electronics operating in harsh radiation environments such as outer space and nuclear energy industries. In this work, radiation-hardened solution-processed ZrLaO thin films are demonstrated. The radiation effects on solution-processed ZrLaO thin films and InOx/ZrLaO TFTs were systemically investigated. The Zr0.9La0.1Oy thin films demonstrated excellent radiation hardness with negligible roughness, composition, electrical property, and bias-stress stability degradation after radiation exposure. The metal-oxide-semiconductor capacitors (MOSCAPs) based on Zr0.9La0.1Oy gate dielectrics exhibited an ultra-low flat band-voltage (VFB) sensitivity of 0.11 mV/ krad and 0.19 mV/ krad under low dose and high dose gamma irradiation conditions, respectively. The low dose condition had a 103 krad (SiO2) total dose and a 0.12 rad/s low dose rate, whereas the high dose condition had a 580 krad total dose and a 278 rad/s high dose rate. Furthermore, InOx/Zr0.9La0.1Oy thin film transistors (TFTs) exhibited a large Ion/Ioff of 2 × 106, a small subthreshold swing (SS) of 0.11 V/ dec, a small interface trap density (Dit) of 1 × 1012 cm-2, and a 0.16 V threshold shift (ΔVTH) under 3600 s positive bias-stress (PBS). InOx/Zr0.9La0.1Oy TFTs based resistor loaded inverters demonstrated complete swing behavior, a static output gain of 13.3 under 4 V VDD, and a ~ 9 % radiation induced degradation. Through separated investigation of the radiation-induced degradation on the semiconductor layer and dielectric layer of TFTs, it was found that radiation exposure mainly generated oxygen vacancies (Vo) and increased electron concentration among gate oxide. Nevertheless, the radiation-induced TFT instability was mainly related to the semiconductor layer degradation, which could be possibly suppressed by back-channel passivation. The demonstrated results indicate that solution-processed ZrLaO is a high-potential candidate for large-area electronics and circuits applied in harsh radiation environments. Besides, the detailed investigation of radiation-induced degradation on solution-processed high-*k* dielectrics in this work provided clear inspiration for developing novel flexible rad-hard dielectrics.

**Keywords: *Solution-processed; High-k gate oxide; Zirconium oxide; Lanthanum oxide; Radiation hardness; Inverter.***

## Introduction

Advanced electronic devices and integrated circuits (ICs) are crucial for applications working in nuclear energy industries and space, leading to the increased demand for transistors with excellent radiation hardness in recent years.1-4 Solution-process is a promising thin film deposition method for large-area rad-hard applications such as wearable X-ray detectors,5 antenna arrays, and flexible materials6 for space suits or robots.7 Compared to traditional methods, the advantages of the solution-process are simple, low-cost, atmospheric processable, and high throughput.8-10 As a result, solution-process is appropriate for large area flexible thin film transistors (TFTs) fabrication. For portable and battery-powered electronics working in space environments, high-*k* dielectrics are preferred due to their energy-saving ability (low operation voltage, low power consumption) compared to traditional SiO2.11, 12 ZrO2 is a potential candidate with relatively low interface trap density, high dielectric constants (~ 22), and suitable band alignment.13-15 In recent years, La2O3 has attracted much attention due to its high *k* value (~ 27), large bandgap (5.8~6.0 eV), high breakdown field, and good thermodynamic stability.16-18 Through combining Zr and La, it is possible to suppress the water and carbon absorption, and the crystallization of thin films.19, 20

Some applications working in harsh radiation environments suffered from space-like radiation with a 10-2-10-6 rad/s relatively low dose rate. Therefore, the detailed investigation of low-dose-rate radiation effects on solution-processed high-*k* dielectrics is critical to analyze the device degradation in harsh space environments and the improvement of rad-hard devices. Currently, laboratories employ gamma-ray radiation sources to evaluate and predict the radiation-induced degradation of devices operating under space-like environments.21 Radiation could damage the semiconductor layer, gate dielectrics, and surrounding insulators, including the isolation or substate oxide.22 For devices fabricated by vacuum methods, radiation-induced charge trapping/de-trapping behaviors among dielectrics of transistors dominate the device degradation.23 Generally, oxygen vacancies could lead to increased electron concentration under radiation exposure and are responsible for the radiation-induced degradation in high-*k* oxides.24 Investigation on Al2O3 deposited by ALD has shown that the gamma irradiation on thin-film caused significant oxygen vacancy formation and barrier height reduction.25 Nevertheless, to the best of our knowledge, the radiation-induced degradation of solution-processed high-*k* dielectrics has been seldomly investigated and reported.24 This study aims to explore the applications of radiation-hardened solution-processed ZrLaO dielectrics in TFTs and inverters working in harsh radiation environments. Solution-processed ZrLaO thin films and InOx/ZrLaO TFTs with different La corporations were fabricated. The InOx/Zr0.9La0.1Oy TFTs had an Ion/Ioff up to ~ 2🞨106, a small subthreshold swing (SS) of ~ 0.11 V/dec, and the resistor-loaded inverter based on InOx/Zr0.9La0.1Oy TFTs exhibited a high output gain ~ 13.3 at 4 V working voltage. Notably, the radiation effects on the composition, surface roughness, and electrical properties of ZrLaO thin film were systemically investigated. The metal-oxide-semiconductor capacitors (MOSCAPs) based on Zr0.9La0.1Oy gate dielectrics exhibited an ultra-low flat band-voltage (VFB) sensitivity of 0.11 mV/ krad and 0.19 mV/krad under low dose and high dose gamma irradiation conditions. The low dose condition had a 103 krad (SiO2) total dose and a 0.12 rad/s low dose rate, whereas the high dose condition had a 580 krad total dose and 278 rad/s high dose rate. As shown in **Figure 1**, compared to previously reported devices,26-30 the VFB sensitivities of Zr0.9La0.1Oy MOSCAPs are promising values for radiation-hardened applications. Whereas the radiation-induced degradation on the dielectric layer and semiconductor layer of InOx/ZrLaO TFTs was investigated in separation. The demonstrated results indicate that solution-processed ZrLaO dielectrics have high potential for large-area electronics applied in harsh radiation environments. Besides, the detailed investigation of radiation-induced degradation on solution-processed high-*k* dielectrics could provide a clear inspiration for developing novel flexible rad-hard dielectrics.

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| **Figure 1.** Summarized flat-band voltage (VFB) sensitivity of high-*k* dielectrics under irradiation in recent years.26-30 |

## Results and discussion

### Precursor and thin film properties

The thin film fabrication and characterization details are introduced in the experimental methods section. **Figure 2 (a)** is a schematic diagram of gamma-irradiation on ZrLaO thin films and devices. **Figure 2 (b)-(d)** demonstrate the atomic force microscope (AFM) results of fresh ZrLaO thin films with different La incorporation. The calculated root-mean-square (RMS) values of Zr-only, Zr0.9La0.1Oy, and Zr0.8La0.2Oy thin films are 0.195, 0.133, and 0.141 nm, respectively. The small RMS values are related to the amorphous structure of ZrLaO thin films and the utilization of organic free de-ionized (DI) water as the precursor solvent.31 **Figure 2 (e)-(g)** display the AFM images of ZrLaO thin films after 144 krad γ-ray irradiation, and the RMS values of Zr-only, Zr0.9La0.1Oy, and Zr0.8La0.2Oy thin films are 0.282, 0.117, and 0.143 nm, respectively. **Table S1** in supplementary documents summarized the RMS values of the thin films. The Zr-only thin films exhibited an increased surface roughness after irradiation compared to fresh thin films, corresponding to some small peaks generated by the high-energy photon colliding with the metal-oxide and the change of thin-film physical structures.7 On the other hand, the RMS values of thin films with La incorporation are almost the same before and after irradiation, which is probably related to the dense film and relatively high La-O bond dissociation energy. As the radiation exposure was carried out in ambient air. The ZrLaO thin films were also exposed to ambient air for 5 weeks to investigate the ambient air effect during radiation exposure, as shown in **Figure S1**. Compared to the fresh thin films, there is no significant variation of surface roughness of all thin films, demonstrating satisfied moisture resistance.9

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| **Figure 2. (a)** Schematic diagram of gamma-irradiation on ZrLaO thin films and devices. 3D atomic force microscopy (AFM) results of ZrLaO thin films with different La concentrations **(b)-(d)** before and **(e)-(g)** after 144 krad (SiO2) irradiation. |

To analyze the composition variation induced by irradiation and ambient air exposure, X-ray photoelectron spectroscopy (XPS) characterization was carried out, as shown in **Figure 3**.284.6 eV C 1s reference was utilized to calibrate all peaks, Gaussian–Lorenz fitting method was used to deconvolute the spectra based on Shirley type background. **Figure 3 (a)-(c)** display the divided O 1s peaks of ZrLaO thin films after 144 krad, including three peaks centered at 529.5 (OI), 531.1(OII), and 532.1 eV (OIII), respectively. The O 1s peak deconvolutions of ZrLaO thin films before and after 5 weeks ambient air exposure are displayed in **Figure S2** for comparison. OI peak represents O2- ions combined with Zr and La ions, OII peak is assigned to O2- ions in the oxygen-deficient regions such as oxygen vacancy (Vo), and OIII peak is related to loosely bound oxygen, such as -CO3, absorbed O2 or H2O.32 33

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| **Figure 3. (a)-(c)** X-ray photoelectron spectroscopy (XPS) spectra of O 1s narrow scans. Summarized atomic percentages of ZrLaO thin films with different La concentrations **(d)** before irradiation, **(e)** after 144 krad irradiation exposure, and **(f)** after 5 weeks ambient air exposure. |

**Figure 3** **(d)** summarizes the calculated atomic percentages based on O 1s peaks deconvolution, with La content increasing from 0 to 10 %, the OI peak percentage (OI/Ototal) of the total oxygen region increased from 62.9 % to 66.7 % and the OII peak percentage (OII/Ototal) decreased from 23.2 % to 18.8 %. **Table S1** summarizes the atomic ratio of ZrLaO thin films under different conditions. The results suggest that appropriate La doping (10 %) could reduce bonded oxygen density, especially Vo, and maximize the metal-oxide framework formation. La has higher oxygen bond dissociation energy (798 kJ mol−1) with O than Zr (766 kJ mol−1), which may be helpful to lower down and control the total Vo amount. However, when the La content increased to 20 %, the OI/Ototal decreased from 66.7 % to 64.5 %, OIII/Ototal increased from 14.4 % to 18.8 %, which was probably attributed to the poor densification and incomplete dehydration of the high-La samples at low temperature.34 The thin film compositions after radiation exposure are summarized in **Figure 3 (e)**; the Zr-only thin films exhibited a significant variation of composition and peak shape. After photon irradiation, M-O-M peak decreased notably, whereas the Vo and M-O-H peaks increased significantly.

As discussed before, when metal-oxide thin film suffered from high-energy photon collision, Vo could be generated and act as shallow donor states or deep traps. In addition, Vo could form hydroxides after adsorbing moisture. The Zr0.9La0.1Oy thin films exhibited a less increase of Vo concentration compared to Zr-only films after irradiation; the improved radiation hardness is due to the large Vo generation energy of the La2O3 suppressed the vacancy generation. It is reported that doping is an effective way to suppress radiation-induced damage.2 However, when La incorporation continues to increase to 20 %, the thin film radiation hardness degraded. The M-OH concentration increased slightly after 144 krad radiation exposure, which is possibly ascribed to the irradiation enhanced moisture absorption of La2O3, the detailed mechanism requires further investigation. Notably, radiation hardness can be improved by optimizing the La2O3 content (~10 %) doped in ZrO2. **Figure 3 (f)** summarizes the atomic percentages of ZrLaO thin films after 5-weeks ambient air exposure and the concentration of M-O and M-OH of all films exhibited no significant variation. As a result, the composition variations difference between **Figure 3 (d)** and **(e)** is mainly caused by radiation exposure. The XPS results indicate that doping appropriate amount of La2O3 (~ 10 %) into ZrO2 is an appropriate solution to enhance the radiation hardness of ZrLaO thin films.

### Electrical properties of ZrLaO thin films

To further determine the radiation-induced property degradation of ZrLaO thin films, ZrLaO metal-oxide-semiconductor capacitors (MOSCAPs) were fabricated and characterized. According to the high radiation tolerance of Zr0.9La0.1Oy thin films demonstrated by AFM and XPS results, **Figure 4 (a)** displays the capacitor-voltage (C-V) curves of Al/ Zr0.9La0.1Oy /n+ Si/Al MOSCAPs measured under total ionizing dose (TID) up to 103 krad. The inset shows the structure of a MOSCAP. The hysteresis and flat-band voltage (VFB) of the C-V curves remained stable after irradiation. To investigate the radiation-induced trapping/de-trapping behaviors among the MOSCAPs, the flat-band voltage shift (ΔVFB), oxide trap variation (ΔNot), and interface trap variation (ΔNit)as a function of TID were calculated and summarized in **Figure 4 (b)**. Besides, the radiation hardness of Zr0.9La0.1Oy MOSCAPs under high dose irradiation exposure was investigated and shown in **Figure S3**. The irradiation with a low dose rate of 0.12 rad/s and a high dose rate of 278 rad/s could barely affect the properties of MOSCAPs. Only small ΔVFB (low dose: 0.01 V, high dose: 0.11 V) and ΔNot (low dose: -1.56 × 1010 cm-2, high dose: -2.9 × 1011) were observed, which is far below the maximum tolerance of radiation-induced threshold voltage shift (ΔVTH < 0.3 V) of commercial Si-based ICs,35 indicating the satisfied radiation hardness of solution-processed Zr0.9La0.1Oy thin films.

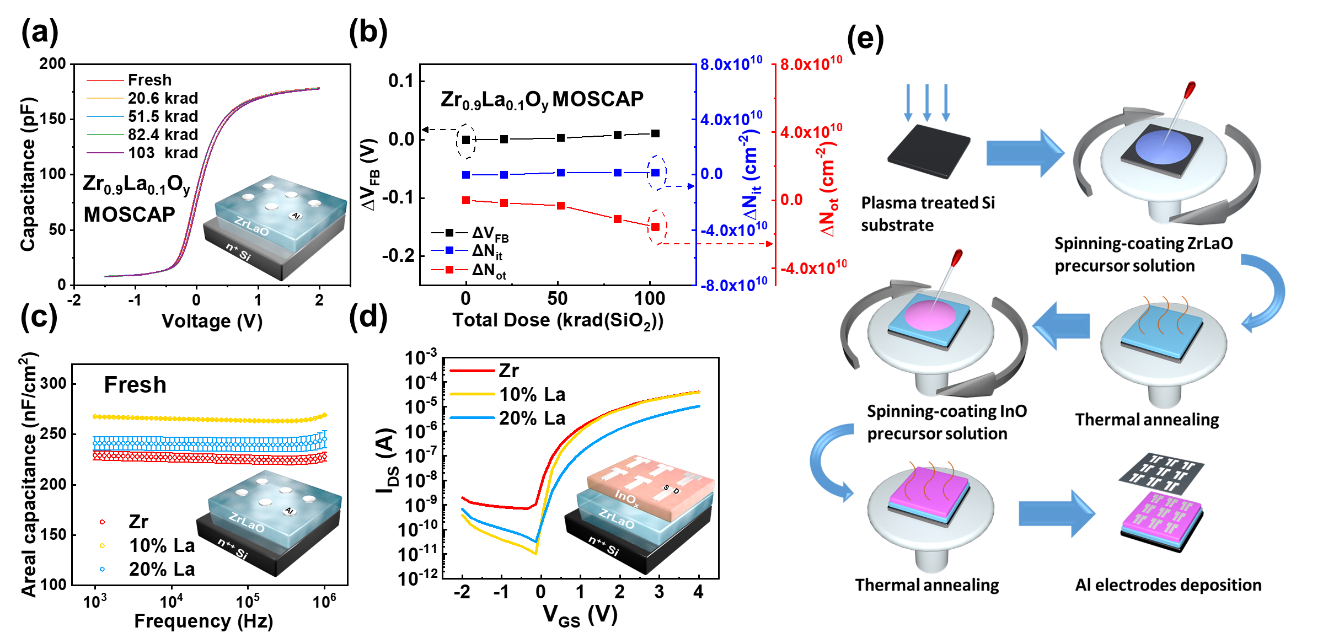
To investigate the electrical properties of ZrLaO thin films, metal-insulator-metal capacitors (MIMCAPs) were fabricated and the parameters were summarized in **Table 1**. **Figure 4 (c)** shows the frequency-dependent areal capacitance of fresh ZrLaO thin films, and the inset displays the structure of MIMCAPs. The leakage behaviors are displayed in **Figure S4 (a),** and the ambient air stability of MIMCAPs was investigated in **Figure S4 (b)** and **(c)**. The *k* values at 1 kHz as a function of La content (0%, 10%, 20%) were calculated to be 11, 16.4, and 18.2, respectively. The increased *k* value is ascribed to the higher *k* value of La2O3 (~ 27) than ZrO2 (~ 22). Besides, the Zr0.9La0.1Oy MIMCAPs exhibited the weakest frequency dispersion of capacitance in all frequency regions and the best ambient air stability, indicating the gradual decomposition of impurities and defects in Zr0.9La0.1Oythin films, and the generation of a high-quality metal-oxide network.36

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| **Table 1.** Dielectric properties of solution-processed ZrLaO thin films.   |  |  |  |  |  | | --- | --- | --- | --- | --- | |  | **Thickness**  **(nm)** | **Leakage current (A/cm2) at 2.5 MV/cm** | **Areal capacitance (nF/cm2) at 1 kHz** | **Dielectric Constant at 1 kHz** | | **Zr-only** | 50.2 | Breakdown | 269 | 11.0 | | **Zr0.9La0.1Oy** | 61.3 | 2.2×10-7 | 241 | 16.4 | | **Zr0.8La0.2Oy** | 73.3 | 2.4 ×10-7 | 229 | 18.2 | |

### The properties of ZrLaO based TFTs and inverters

#### TFT parameters

To explore the applications of ZrLaO films in low power electronics, TFTs based on ZrLaO gate dielectrics were fabricated, and the fabrication process is demonstrated in **Figure 4 (e)**. **Figure 4 (d)** displays the typical transfer characteristics (IDS-VGS) measured at drain voltage VDS = 3.5 V, and the inset is the TFT structure. The main TFTs device parameters and their distributions are summarized in **Table 2** and **Figure S5**; at least 5 devices were measured for each La concentration to ensure the data authenticity. The operation voltage of InOx/ZrLaO TFTs is down to 4 V, which is ultra-low compared to those of TFTs based on SiO2,9, 37 such a low operation voltage indicates the potential applications of ZrLaO based TFTs in low power consumption electronics. The large Ion/Ioff, small SS, and small Dit values demonstrated the feasibility of Zr0.9La0.1Oy thin film as the gate oxide for InOx TFTs. The small SS values for InOx/Zr0.9La0.1Oy TFTs is possibly ascribed to the large areal capacitance of the Zr0.9La0.1Oy gate oxide and the high-quality InOx/Zr0.9La0.1Oy interface. The Dit value of the InOx/Zr0.9La0.1Oy TFT is comparable to those based on other solution-processed high-*k* dielectrics, e.g., AlOx (2.6 × 1012 cm−2),38 YOx (2.7 × 1012 cm−2),39 MgOx (9 × 1012 cm−2),40 and ScOx (3 × 1012 cm−2).31 Besides, the calculations of activation energy (Ea) and density of states (DOS) are shown in **Figure S6,** indicate that the InOx layers fabricated on different ZrLaO thin films have almost the same property and the improvement of TFTs performance is related to the La doping in the dielectric layer. On the other hand, excessive La concentration (20 %) could decrease Ion and poor InOx/ZrLaO interface. It is reported that Vo among oxide could act as trap defects and degrade the properties of the device.41 According to the XPS results, the decrease in Vo is responsible for the reduced current of the device after 20 % La doping, while the increase of metal hydroxide related groups resulted in the increased InOx/ZrLaO interface trap densities.



**Figure 4.** **(a)** Capacitance-voltage (C-V) curves and **(b)** summarized ΔVFB, ΔNot, and ΔNit of Zr0.9La0.1Oy metal-oxide-semiconductor capacitors (MOSCAPs) after 103 krad irradiation exposure. **(c)** Capacitance-frequency (C-f) curves of ZrLaO metal-insulator-metal (MIM) devices, the inset is the device structure. **(d)** Transfer characteristics (IDS-VGS) of InOx/ZrLaO thin film transistors (TFT), inset is the device structure. **(e)** The fabrication process of InOx/ZrLaO TFTs.

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| **Table 2.** Electrical parameters of InOx/ZrLaO TFTs with different La concentrations.   |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | | La content | (cm2 V-1 s-1) | Ion/Ioff | VTH  (V) | SS  (V/ dec) | Dit  (🞨1012 cm-2) | | Zr-only | 1.7 ± 0.27 | ~ 1🞨105 | 0.42 ± 0.17 | 0.27 ± 0.12 | 5.5 ± 3.0 | | 10% La | 2.2 ± 0.06 | ~ 2🞨106 | 0.59 ± 0.16 | 0.11 ± 0.01 | 1.0 ± 0.3 | | 20% La | 0.9 ± 0.28 | ~ 3🞨105 | 0.77 ± 0.18 | 0.26 ± 0.09 | 4.8 ± 2.1 | |

#### TFT properties and bias stress (BS) stability degradation before and after irradiation

To investigate the radiation hardness of ZrLaO based TFTs, the transfer characteristics were measured under different TID, as shown in **Figure 5 (a)**. The summarized Ion/Ioff and VTH as a function of TID are displayed in **Figure 5 (b)** and the detailed TFT parameters after 103 krad are shown in **Table S2**; there is a slight decrease of Ion/Ioff value and an increase of VTH, revealing the excellent radiation hardness of InOx/Zr0.9La0.1Oy TFTs under a low dose rate environment. When considering display applications, the operational reliabilities TFTs are crucial electrical parameters. The InOx/Zr0.9La0.1Oy TFTs have demonstrated the best devices properties, and their positive bias stress (PBS) stability with stress time up to 3600 s are investigated in **Figure 5 (c)**. +2 V gate bias was applied to the gate of TFTs with their source and drain grounded during the bias. The inset shows the relationship between voltage shift (ΔVTH) and stress time (t). A stretched exponential model with the following equation (1) can be utilized to fit the ΔVTH:42

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|  | (1) |

where ΔVTH0 is the ΔVTH at infinite time, is the carrier characteristic de-trapping time, and is the stretched exponential exponent. The ΔVTH as a function of stress time fitted the stretched exponential model, indicating that the dominant degradation mechanism is the charge trapping behavior at the TFT channel.43 The 0.16 V small ΔVTH corresponded to the enhanced InOx/ZrLaO interface with a small Dit value. The relatively parallel VTH shift and insignificant SS value variation suggested the semiconductor/dielectric interface had negligible bias-stress induced defects during the measurements.31

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| **Figure 5. (a)** IDS-VGS before and after 103 krad irradiation. **(b)** Ion/Ioff and VTH as a function of the total dose. **(c)** Positive bias-stress (PBS) stability of InOx/Zr0.9La0.1Oy TFTs, inset is the exponential fitting of ΔVTH under 3600 s PBS. **(d)** PBS stability of InOx/Zr0.9La0.1Oy TFT after 103 krad irradiation. **(e)** Exponential fitting of ΔVTH under 500 s PBS after 103 krad and 10 days. **(f)** Summarized ΔVFB, ΔNot, and ΔNit under 1000 s bias stress of Zr0.9La0.1Oy MOSCAPs before and after 103 krad irradiation. |

To testify the effect of radiation on the PBS stability of InOx/Zr0.9La0.1Oy TFTs, the PBS stability after irradiation was investigated in **Figure 5 (d)**. The summarized VTH after 103 krad irradiation exposure and 10 days ambient air exposure are shown in **Figure 5 (e)** for comparison. The radiation may have induced Vo to increase the electron concentration, which is reflected by the increased ΔVTH, compared to the ΔVTH of air-exposed devices in **Figure 5 (e)**. The positive ΔVTH after irradiation is mainly due to the enhanced oxygen adsorption of the InOx layer. Generally, back-channel adsorbing gas molecules is one of the instability factors of oxide TFTs, which would be discussed later in detail. To separate the radiation-induced degradation of the dielectric layer and semiconductor layer, the BS stability of Zr0.9La0.1Oy MOSCAPs before and after irradiation was investigated. **Figure 5 (f**) displays the summarized ΔVFB, ΔNot, and ΔNit under 1000 s PBS before and after 103 krad irradiation. Without the radiation-induced degradation of the InOx layer. The Zr0.9La0.1Oy thin films exhibited negligible BS stability degradation due to radiation exposure. After irradiation, PBS could induce insignificant positive ΔVFB and ΔNot in Zr0.9La0.1Oy thin films compare to the pre-radiation results, which is probably caused by the radiation-induced net proton (H+) related positive charges.

#### InOx/ZrLaO TFT based inverter

As InOx/Zr0.9La0.1Oy TFTs have demonstrated excellent performance and radiation hardness, we further explored their application in inverter. By connecting InOx/ZrLaO TFTs and a 13 MΩ resistor in series, a resistor-loaded inverter was achieved. **Figure 6 (a)** and **Figure S7** exhibit the voltage transfer characteristic (VTC) curves and voltage gain (−∂Vout/∂Vin) of inverters under 1 to 4 V VDD, the inset shows the connection circuit of the inverter. The inverters exhibited complete swing characteristics with output high voltage (VOH) ≈VDD and output low voltage (VOL) ≈ 0 V. The voltage gain is around 13.3 when VDD = 4 V, which is a promising value compared to the inverters reported in the literature, as shown in **Table 3.**10, 44-49 The high voltage gain was ascribed to the balanced mobility, the normally-off features, and the small SS of InOx/Zr0.9La0.1Oy TFTs. The output characteristics and gain of the inverter before and after 103 krad low dose irradiation are shown in **Figure 6 (b)** and **Figure 6 (c)**, respectively. The irradiation only led to a slight output degradation of the inverter; as summarized in **Figure 6 (d)**, the voltage gain decreased around 9 % (13.3 to 12.1), the transition voltage positive shifted around 9 % (0.66 to 0.73 V). The decline of the voltage gain is affected by SS degradation caused by interface traps generation. Meanwhile, the shift of transition voltage is related to the TFTs threshold voltage shift induced by the net positive trapped charges among the gate dielectric and semiconductor layer. As analyzed in **Figure 5 (f)**, the degradation of the inverter is mainly related to the instability of the InOx semiconductor layer. The results suggested that InOx/Zr0.9La0.1Oy TFTs have satisfied radiation hardness, and the 103 krad irradiation exposure could barely degrade the TFT properties.

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| **Table 3.** Voltage gain of different inverter circuits based on different TFTs.   |  |  |  |  |  | | --- | --- | --- | --- | --- | | **Semiconductor/ Dielectric** | **VDD (V)** | **Gain** | **Year** | **reference** | | **IZO&GIZO/paper** | 15 | 4.7 | 2011 | 44 | | **In2O3/SrOx** | 4 | 9.7 | 2017 | 45 | | **In2O3/Yb2O3** | 4 | 10.6 | 2017 | 46 | | **In2O3/Al2O3** | 3 | 5 | 2018 | 10 | | **In2O3/ZrGdOx** | 2.5 | 7.4 | 2018 | 47 | | **LiInO/AlO** | 3 | 6 | 2020 | 48 | | **IGZO/SiO2** | 10 | 6.8 | 2020 | 49 | | **InOx/ZrLaO** | **4** | **13.3** | **2021** | **This work** | |

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| **Figure 6.** Characteristics of 13 MΩ resistor-loaded inverters based on InOx/Zr0.9La0.1Oy TFTs. **(a)** Typical voltage transfer characteristic (VTC) and voltage gain, the inset is the circuit of the inverter. **(b)** VTC curves at VDD = 4 V and **(c)** Vin dependent voltage gains before and after irradiation. **(d)** The voltage gain and transition voltage variation as a function of total dose up to 103 krad. **(e)** The schematic diagram of the radiation exposure and oxygen adsorption induced degradation of InOx/ZrLaO TFTs. |

**Figure 6** **(e)** demonstrates the schematic diagram of radiation effects on InOx/ ZrLaO TFT. As reported, radiation could lead to the formation of shallow donors in gate oxide, passivation of band tail state, a negative shift of VTH, and an increase of mobility.7 However, a decreased mobility and positive VTH shift were observed in ZrLaO TFTs, indicating that the ambient air effect dominated the device degradation. The oxygen molecules adsorption at the surface of back-channel follows chemical equilibrium equation:50

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|  | (2) |

where K is the equilibrium constant, is the adsorbed oxygen concentration at back-channel surface, is the oxygen partial pressure and n is the electron density in InOx semiconductor thin film. K and are constants at a fixed temperature, the radiation exposure could increase n according to the following equation:51

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|  | (3) |

where Vo is a non-conducting deep state and Vo2+ state provides two delocalized free electrons. Consequently, the increased under radiation exposure and further resulted in the accelerated O2 adsorption at the back-channel. The oxygen molecules have extremely high electronegativity (3.44), they could attract electrons in the InOx film to form oxygen radicals, as described in the equation.50

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|  | (4) |

As a result of oxygen adsorption, a depletion layer was formed beneath the InOx surface, leading to decreased carrier concentration. Therefore, a higher gate voltage was required to turn on the InOx/ZrLaO TFTs, and VTH was positively shifted. Radiation could also generate electron-hole pairs (EHPs) when passing through the gate oxide.52 With a positive applied electrical field, the electrons transported out of ZrLaO thin film in picoseconds, some fraction of the electrons recombined with holes in the oxide valence band even before they left the oxide. Those holes that escaped from the recombination transported through ZrLaO and be trapped at the InOx/ZrLaO interface to form an interface trap, and the TFT mobility was decreased accordingly. The transportation was accompanied by hydrogen releasing, in the form of H+. The released H+ moved towards the InOx/ZrLaO interface and were trapped by the defects among the ZrLaO thin films to form radiation-induced positive traps, which contributed to the positive VTH shift.

For further investigation, the device mobility and SS degradation enhanced by irradiation exposure could be efficiently suppressed by passivating the backchannel.53 [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) has been reported to be a suitable candidate to stabilize the device, which could control the Fermi level of the films by acting as a remote dopant layer.7 Besides, an organic semiconductor above the oxide surface is helpful to suppress Vo generation and regenerate broken bonds, due to the formation of saturated unfilled coordination at the oxide surface.7

## Conclusion

In summary, the effect of gamma irradiation on solution-processed ZrLaO thin films and InOx/ZrLaO TFTs was investigated. The characterization results indicated that Zr0.9La0.1Oy films annealed at 350 °C had high M-O concentration, low Vo density, small frequency dispersion, and a large breakdown electrical field. The MOSCAPs based on Zr0.9La0.1Oy gate dielectrics exhibited an ultra-low VFB sensitivity of 0.11 mV/ krad and 0.19 mV/krad under low dose and high dose gamma irradiation conditions, respectively. The low dose condition had a 103 krad (SiO2) total dose and a 0.12 rad/s low dose rate, whereas the high dose condition had a 580 krad total dose and 278 rad/s high dose rate. InOx/ZrLaO TFTs exhibited high performance of a large Ion/Ioff of 2 × 106, a small SS of 0.11 V dec-1, a small Dit of 1 × 1012 cm-2, and a ΔVTH of 0.16 V under 3600 s PBS. Besides, InOx/Zr0.9La0.1Oy TFTs based resistor loaded inverters demonstrated complete swing characteristics and a high gain of 13.3 at VDD = 4 V. Notably, the surface roughness, composition, electrical properties, bias-stress stability of Zr0.9La0.1Oy thin films had no significant variations after 103 krad low dose irradiation. It is found that radiation exposure mainly generated Vo among ZrLaO thin films and increased the mobility of the TFT devices. Doping La into ZrO2 had demonstrated better thin film radiation hardness, due to the higher La-O bond dissociation energy than Zr-O bond, and the suppressed Vo generation among the bulk oxide. Compared to the irradiation effect, the oxygen adsorption at the back-channel caused by ambient air exposure dominated the degradation of the TFTs, which should be suppressed by back-channel passivation of the back-channel. Overall, the Zr0.9La0.1Oy thin films without passivation have demonstrated satisfied radiation hardness, which is crucial to the realization of large-area rad-hard applications such as wearable X-ray detectors,5 antenna arrays, and flexible materials6 for space suits or robots.7

**Experimental Methods**

**Precursor Solution Preparation**

To prepare 2.00 M (total metal, Zr: La=10:0, 9:1 and 8:2) ZrLaO precursor solution, zirconium oxynitrate hydrate (ZrO(NO3)2·xH2O, 99.5 %) was dissolved in de-ionized (DI) H2O. Followed by a vigorous stirring of the solution at ∼70 °C. After complete dissolution, lanthanum nitrate hexahydrate (LaN3O9·6H2O, 99.9 %) was added to the solution with dissolved ZrO(NO3)2·xH2O for further 8h heating and stirring. To prepare 0.1 M InOx precursor solution, indium nitrate hydrate (In(NO3)3∙xH2O, Aladdin) was dissolved in DI water and the solution was vigorously stirred at room temperature for 2 h. All precursor solution was then filtered by a 0.2 μm polytetrafluoroethylene (PTFE) syringe filter before spinning coating.

**Thin Film Preparation and Characterization**

To prepare the substrates, heavily doped and lightly doped (orientation:100, doping concentration: ~1015 cm-3, resistivity: 2-4 Ω·cm) n-type Si substrates were dipped in 2% HF aqueous solution for 60 s to remove the native oxide and then dried by N2. ZrLaO precursor solution was dropped onto cleaned Si substrates and spun at 3000 rpm for 30 s. Then the substrates were placed on a 125 °C hot plate, the temperature was linearly increased to 350 oC with a heating rate of 25 oC min-1 and held for 1 h. The surface morphologies of the ZrLaO thin films were investigated by AFM. The compositions of the ZrLaO thin films were determined by XPS. For radiation hardness investigation, a 662-keV Cs137 γ-ray radiation source was used for low dose measurement, the stress time was up to 14 days and the total dose was up to 144 krad (SiO2) at a dose rate of 0.12 rad s-1. For high dose measurements, a Co60 γ-ray radiation source was used, the total dose was up to 580 krad with a dose rate of 278 rad/s.

**Device Fabrication and Characterization**

InOx precursor solution was dropped onto the deposited ZrLaO thin films and spun at 3000 rpm for 20 s. After that, the samples were heated at 250 oC for 1h on a hot plate. Finally, shadow masks were used to deposit 300 nm thick Al source, drain, and bottom electrodes through e-beam evaporation. The ratio of channel width (W = 150 μm) and length (L = 10 μm) was defined as 15. To investigate the electrical properties of ZrLaO dielectrics, Al/ZrLaO/n+ Si metal-oxide-semiconductor capacitors (MOSCAPs) and Al/ZrLaO/n++ Si metal-insulator-metal capacitors (MIMCAPs) were prepared with d = 0.3 mm diameter circular top Al electrode. The electrical characteristics of ZrLaO capacitors and InOx/ZrLaO TFT were investigated by the semiconductor device analyzer (Agilent B1500A) in a dark shelter at room temperature.

The VTH of TFT was determined by linear fitting to the dependence of IDS1/2 on VGS. The saturation carrier mobility (*)* was extracted by the following formula20:

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| --- | --- |
|  | (5) |

where VGS is the gate voltage, is the saturation current and Ci is the areal capacitance of MIM capacitors. Dit was calculated using the following equation:40

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| --- | --- |
|  | (6) |

where SS is the subthreshold swing, q is the electron charge and k is the Boltzmann constant. To investigate the BS stability of the InOx/ZrLaO TFTs, a constant gate bias was applied on the gate while the source and drain electrodes were grounded. The IDS=VGS curves of the InOx/ZrLaO TFTs under PBS were measured in the dark environment and the stress time was up to 3600 s. To investigate the radiation hardness of InOx/ZrLaO TFTs, transfer curves were characterized before and after γ-ray irradiation to analyze the radiation-induced degradation. Considering the irradiation exposure was carried out in ambient air, the devices' property degradation under ambient air exposure was investigated for comparison.

## Associated content

### Supporting information

AFM and XPS results of ZrLaO thin films before and after 5-weeks ambient air exposure, summarized RMS value and atomic ratio of ZrLaO thin films under different conditions, C-V curves and summarized ΔVFB, ΔNot and ΔNit of Zr0.9La0.1Oy MOSCAPs under high dose condition, C-V, J-E of ZrLaO MOSCAPs before and after 5-weeks ambient air exposure, the distribution of InOx/ZrLaO TFT parameters, activation energy (Ea) as a function of VGS for various TFT devices, VTC, voltage gain and linear fit of inverters based on InOx/ZrLaO TFTs, electrical parameters of InOx/Zr0.9La0.1Oy TFTs after 103 krad irradiation.

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