Bias-stress-stable Sub-1.5 V Oxide Thin-film Transistors via Synergistic Composition of Sol-gel Quaternary High-k Oxide Dielectrics

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Abstract

A rising demand in reliable, energy-efficient, and large-area electronics, particularly in the realm of sol-gel oxide thin-film transistors (TFTs), has steered research focus away from semiconductor towards dielectrics. However, achieving both bias stability and low-voltage operation remains a significant hurdle. While typical oxide TFTs employ high-dielectric-constant (high-$k$) dielectrics with lowered film thickness to acquire low-voltage operation, they inevitably suffer from undesired defects at both bulk and interfacial trap sites in dielectric layer. In this study, bias-stress-stable all solution-processed oxide TFTs were demonstrated with operation voltage under 1.5 V via sol-gel quaternary high-$k$ oxide dielectric (Al-Hf-Zr-O, AHZO). In-depth understanding of their individual contributions to dielectric performance leads to the acquisition of optimized composition ratios of AHZO with amorphous feature and outstanding dielectric performance, marked by dielectric constant ($k$) over 11, leakage current density ($J_{\text{leak}}$) below $10^{-5.5}$ A cm$^{-2}$, and sturdy breakdown strength ($E_B$) exceeding 5 MV cm$^{-1}$. By integrating the AHZO with In-Ga-Zn-O (IGZO) layer, we achieved sub 1.5 V TFTs while maintaining excellent bias stability with threshold voltage ($V_{\text{TH}}$) shift lower than 0.20 V for 3600 s. Our findings offer a detailed insight into the realm of multi-component oxide dielectrics, paving the way for miniaturization and reliability in functional devices and sensors.

1. Introduction

Sol-gel-derived oxides have shown great potential in flexible and transparent electronics such as thin-film transistors (TFTs), rivaling the performance of silicon-based CMOS electronics[1–4]. Contrast to vacuum deposition techniques, solution chemical synthesis method has proven offering uniform and large-area deposition with affordable cost as well as facile composition control via a streamlined synthetic route. In–Ga–Zn–O (IGZO), obtained by diverse composition screening of binary oxide semiconductors, has attracted substantial interests in electronics fields for its exceptional carrier mobility, attributed to the spatial expanding of isotropic spherical shapes of metal ns orbitals[5]. Nevertheless, a bias stability issue of sol-gel-derived oxide TFTs impede their practical applications such as degraded image resolution in displays[6, 7], diminished sensor accuracy[8, 9], and restricted reliability of integrated systems[10–12]. In response to these challenges, ongoing research and development have made significant strides in modulating oxide semiconductors, including the realization of defect-free highly ordered crystalline structure[13, 14], and the minimization of trap sites through the use of stacked and/or encapsulated channel layers[15–17].

Despite substantial attempts to boost the operational stability of oxide TFTs, inherent bulk defects in the dielectric layer and interfacial defect between semiconductor and dielectric layer lead to operational instability. A primary concern is the occurrence of undesired surface defects such as dangling bonds. Frequently, these defects arise from the incomplete formation of metal-oxygen-metal (M–O–M) networks, leaving bias-reactive hydroxide groups. These hydroxide groups deteriorate the operation stability of sol-gel-derived oxide TFTs by acting themselves as trap sites for charge carriers and affecting dipole momentum for polarization[18]. Another concern is the presence of bulk traps in oxide dielectrics,
such as atomic vacancies, interstitials, or impurities. These bulk traps stem from grain boundaries and/or defects in oxide lattice due to incomplete sol-gel reaction[19, 20]. Those trap sites are particularly troubling as they cause threshold voltage ($V_{TH}$) shifts and severe enlarged hysteresis loop, leading to inconsistent device performance for long-term operation[21].

In addition to the bias stability issue, another key aspect for practical application of oxide TFTs is the energy-efficient operation. To achieve these goals, an employment of physically thin high-dielectric-constant (high-$k$) oxide dielectric layers, such as AlOx, HfOx, ZrOx, and multi-components of ternary oxides (AZO, HZO, AHO, and etc.), is essential for increasing areal capacitance, which in turn allows for a reduction in field-driving voltage and consequent power consumption[22–24]. Nevertheless, the few-tens-of-nanometer thick high-$k$ dielectric layers often exacerbate leakage current, presumably due to the tunneling phenomena and undesired pin-holes[25]. Also, the multi-component oxide system with diverse metals, a promising strategy for acquiring high-$k$, suffered from distinctly different hydrolysis, condensation, and phase-transformation route due to their inherent chemical information[26], resulting in generation of defect sites in metal-oxygen-metal (M-O-M) network. Therefore, developing pin-hole free and densified high-$k$ oxide dielectrics is crucial, not only for enhancing oxide TFT performance but also for fulfilling the energy efficiency requirements of electronic devices.

However, achieving both bias stability and low-voltage operation in sol-gel-derived oxide TFTs remains a significant challenge. The primary difficulty stems from an imbalance between undesired trap sites and incomplete sol-gel reactions within the thin high-$k$ dielectric layer. This leads to films that are unevenly densified, containing detrimental trap sites such as atomic defects and grain boundaries. Such imperfections result in pronounced hysteresis and/or bias instability in TFT applications[27, 28]. Therefore, comprehensive research and a deeper understanding of multi-component oxide dielectrics are crucial to develop oxide TFTs that are both bias-stable and capable of operating at low voltages.

In this study, we presented a systematical investigation of a quaternary oxide dielectric system (Al–Hf–Zr–O, AHZO) aimed at enhancing the bias-stress reliability as well as achieving sub-1.5 V operation of oxide TFTs. The stoichiometric variations in quaternary oxide were identified to understand the individual contributions of each binary oxide to the overall dielectric performance, marked by dielectric constant ($k$), leakage current density ($J_{\text{leak}}$), and breakdown strength ($E_B$) with values of 12.1, $\sim 10^{-6}$ A cm$^{-2}$, and $\sim 5$ MV/cm, respectively. Through detailed analyses, we specified the most advantageous composition ratio of AHZO using stacked triangular phase diagrams and effectively integrated the sol-gel-derived AHZO film with a IGZO layer sequentially. The significance of the AHZO film was highlighted by its amorphous nature, atypical for high-$k$ dielectrics, and its exceptionally smooth surface, which were vital in minimizing the interface trap density and improving the TFT efficacy. The saturation mobility, $V_{TH}$, subthreshold swing (SS), and on/off current ratio ($I_{on}/I_{off}$) of resultant TFTs under the sub-1.5 V operation were 2.95 cm$^2$V$^{-1}$s$^{-1}$, $-0.17$ V, 115 mV dec$^{-1}$, and $\sim 10^6$, respectively. Furthermore, the threshold voltage shifts ($\Delta V_{TH}$) of resultant TFTs with 60 min of positive bias stress (PBS) and negative bias stress (NBS) were lower than 0.2 V and $-0.2$ V, respectively. Our in-depth exploration and
understanding of multi-component oxide dielectrics pave the way for refining their properties to meet the stringent demands of advanced electronics, setting a new benchmark for low-voltage, high-reliability TFT applications.

2. Materials and methods

2.1. Oxide solution synthesis

High purity precursors, including aluminum nitrate nonahydrate (Al(NO$_3$)$_3$•9H$_2$O, 99.997%; Sigma-Aldrich), hafnium chloride (HfCl$_4$, 99%; Alfa Aeser), and zirconium oxynitrate hydrate (ZrO(NO$_3$)$_2$•xH$_2$O, 99.99%; Sigma-Aldrich), were dissolved in 2methoxyethanol (2-ME, CH$_3$OC$_2$H$_4$OH, > 99.0%; TCI) to a stoichiometric concentration of 0.1 m for each solution. These solutions were continuously stirred individually at 60, 25, and 90 °C, respectively, for 24 h under ambient conditions. Subsequently, these binary oxide solutions were blended in arbitrary proportions to prepare the combinatorial oxide solution, followed by stirring at room temperature for 1 h under ambient conditions to ensure homogeneity. The methodology for the preparation of IGZO solutions was in accordance with established protocols detailed in preceding publications[29, 30].

2.2. Device fabrication

The process commenced with heavily doped $n^{++}$-Si wafers serving as gate electrodes. The wafers were cleaned sequentially via ultrasonication in acetone, isopropyl alcohol, and deionized water. Next, they were chemically etched in a dilute hydrofluoric acid solution to remove native oxides. Following etching, the substrates underwent an oxygen plasma treatment to induce hydrophilic surface conditions. The homogenized precursor solutions were then spin-coated onto the substrates at 4000 rpm for 30 s, followed by a soft bake at 70°C for 1 min and a final annealing at 400°C for 90 min on a hot plate. The metal-insulator-metal (MIM) capacitor structure was completed using aluminum electrodes vapor-deposited to a thickness of 100 nm and patterned using a shadow mask to define an area of 0.0009 cm$^2$. For TFT fabrication, the IGZO solution was processed in the same manner as the dielectric layers. Conventional photolithography was used to isolate the layers, followed by the deposition and patterning of Al electrodes. The channel dimensions of the IGZO TFTs were characterized by a width ($W$) and length ($L$) of 800 µm by 150 µm, respectively.

2.3. Physicochemical and electrical characterizations

The crystallographic characteristics of the dielectric layers were investigated using X-ray diffraction (XRD; Rigaku, SmartLab) and transmission electron microscopy (TEM; JEOL, JEM 2100F). The surface morphologies of the dielectric layers were evaluated using atomic force microscopy (AFM; PSIA, XE100). The frequency-dependent areal capacitance was measured using an impedance analyzer (Agilent, E4980A) in the frequency range of 1 to 100 kHz. The leakage current density of the MIM capacitors and the electrical characteristics of the TFTs were measured using a source-meter (Keithley, 4200-SCS) under ambient air and dark conditions. The reliability of the TFTs was tested by applying constant gate
and drain voltages ($V_{GS} = \pm 1.5 \text{ V}$ and $V_{DS} = 0.1 \text{ V}$) for up to 3600 s. The figure-of-merit parameters such as areal capacitance ($C_i$), saturation mobility ($\mu_{sat}$), subthreshold swing ($SS$), and interfacial trap densities ($D_{it}$) were extracted from corresponding devices using established equations:

$$C_i = \frac{k\varepsilon_0}{d};$$

$$\mu_{sat} = \frac{2L}{WC_i} \times \left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}}\right)^2;$$

$$SS = \frac{\Delta V_{GS}}{|\Delta \log I_{DS}|};$$

$$D_{it} = \left[\frac{SS\log (e)}{KT/q} - 1\right] \times \frac{C_i}{q},$$

where $\varepsilon_0$ is the vacuum permittivity, $d$ is the dielectric thickness, $I_{DS}$ is the drain current, $K$ is the Boltzmann constant, $T$ is the temperature, and $q$ is the elementary charge.

3. Results and discussion

3.1. Combinatory oxide dielectrics: from solution synthesis to device fabrication

Figure 1a illustrates an overview of the preparation methodology for sol-gel metal oxide thin films from solution synthesis to film deposition. Before blending the solutions for the quaternary Al–Hf–Zr–O (AHZO), individual precursor solutions were prepared for AlO$_x$, HfO$_x$, and ZrO$_x$ with fixed metal ion concentrations of 0.1 m. Subsequently, we mixed each precursor solution as illustrated in Fig. 1b. This sol-gel synthetic route enables a limitless combination for multi-component oxide whose stoichiometry can be determined by volumetric ratios$^{31, 32}$. Noting that the precise control of stoichiometry in multicomponent oxide films deposited using vacuum- or vapor-based methods remains a challenge$^{33–35}$, this straightforward approach provides an opportunity to modulate their functionalities for desired applications.

To evaluate the dielectric performance of combinatorial AHZO films, we prepared MIM capacitors and TFT devices which employ a sol-gel-derived IGZO as an active layer. Figure 1c illustrates the overall steps of device fabrication. The native oxide (SiO$_x$), generated from the surface oxidation of the Si substrate, has a thickness of few nanometers$^{36}$, was removed before loading the solution to prevent undesired dielectric characteristics. Subsequently, the as-synthesized AHZO solutions were spin-coated atop as-prepared substrates, followed by thermal annealing with the temperature ($T_d$) at 400°C. Because typical oxide solutions contain non-volatile ligands (e.g., nitrate and chloride) and organic solvents (e.g., 2-ME...
and isopropyl alcohol), a high-temperature annealing process is necessary to eliminate various impurities and to form smooth and densified dielectric layer[3, 4]. While the contact metals were directly evaporated atop as-annealed AHZO films for MIM capacitors, an amorphous IGZO layer was deposited onto the dielectric layer in the same manner, followed by thermal evaporation of the source-drain electrodes for bottom-gate top-contact configuration.

3.2. Electrical and material characterizations of binary oxide thin films

Prior to the demonstration of AHZO dielectrics, we fabricated binary oxide based MIM capacitors to verify the inherent characteristics of each oxide component. Figure 2a–c display the plots of $J_{\text{leak}}$ and $k$ for $\text{AlO}_x$, $\text{ZrO}_x$, and $\text{HfO}_x$ capacitors as functions of the electric field and frequency, respectively. For statistical analysis, we measured five individual devices per capacitor (Fig. S1 and S2). From the $C-i$ curves, we extracted the $k$ values of each oxide film at 1 kHz, which were 6.21 ($\text{AlO}_x$), 10.48 ($\text{HfO}_x$), and 17.75 ($\text{ZrO}_x$). Given that solution-processed oxide films inevitably suffer from undesired impurities and defects, the evaluated $k$ values may be lower than their theoretical values[37]. Concerning the different $k$ values, $\text{AlO}_x$ exhibited the lowest values compared to $\text{HfO}_x$ and $\text{ZrO}_x$, which was attributed to the electronegativity difference of the constituent metals[28]. Typically, the ionic bond of a metal oxide tends to have a high dipole moment when the electronegativity of the metal is low, leading to a high $k$. Because the electronegativity of Al is relatively higher than that of Hf and Zr owing to the absence of $d$-state electrons, the $k$ value of $\text{AlO}_x$ is lower than that of the others. Nevertheless, $\text{AlO}_x$ exhibited the lowest $J_{\text{leak}}$ of $\sim 10^{-7}$ A cm$^{-2}$ at 3.0 MV cm$^{-1}$, followed by $\text{HfO}_x$ ($\sim 10^{-6}$ A cm$^{-2}$), and then $\text{ZrO}_x$ ($\sim 10^{-5}$ A cm$^{-2}$). One possible reason is the difference in the bandgap. Note that the bandgaps of $\text{HfO}_x$ and $\text{ZrO}_x$ are lower than that of $\text{AlO}_x$ owing to their $d$-state electrons; the smaller conduction band offset of $\text{HfO}_x$ and $\text{ZrO}_x$ induces an increased $J_{\text{leak}}$[38–40]. This represents a tradeoff between $k$ and $J_{\text{leak}}$ in the binary oxide dielectric. Another probable reason is the different crystallization behaviors. Although $\text{AlO}_x$ exhibited a relatively low $k$, the fully amorphous domain allowed for low and stable $J_{\text{leak}}$ across all electric field ranges.

Figure 2d–f depict the XRD patterns of each binary oxide film with reference peaks for the representative crystalline phases for $\text{Al}_2\text{O}_3$: JCPDS 88–0826 (hexagonal), 86-1410 (monoclinic); for $\text{HfO}_2$, JCPDS 78–0050 (monoclinic), JCPDS 08-0342 (tetragonal); and for $\text{ZrO}_2$, JCPDS 88-1007 (tetragonal), JCPDS 86-1451 (monoclinic)[41–46]. In contrast to $\text{AlO}_x$, we demonstrated that both $\text{HfO}_x$ and $\text{ZrO}_x$ had polycrystalline structures owing to their low crystallization temperatures. As solution-processed binary oxide dielectric films are prone to crystallization during thermal annealing, the grain boundaries inside the film and on the surface lead to the generation of localized states in their forbidden bandgap[18], resulting in a hopping conduction for higher $J_{\text{leak}}$. A detailed polymorph of crystalline binary oxide films was investigated using HR-TEM analysis (Fig. 2g–i). Despite the removal of native oxides, a 3-nm-thick SiO$_x$ layer was incorporated. Consistent with the XRD results, $\text{AlO}_x$ exhibited a fully amorphous domain
whereas HfO<sub>x</sub> and ZrO<sub>x</sub> presented distinct nanocrystal domains. Interestingly, the average size of the ZrO<sub>x</sub> domain was considerably smaller than that of the HfO<sub>x</sub> domain, leading to a frequency-dependent behaviors called dielectric relaxation[47]. The inset images in Fig. 2g–i demonstrate the reciprocal patterns of each binary oxide, obtained by fast Fourier transformation FFT analysis. Indeed, AlO<sub>x</sub> exhibited a noticeably amorphous FFT pattern. However, the most common nanocrystal in HfO<sub>x</sub> was the monoclinic phase oriented along (111) and (–111), for which the d-spacing values were 0.283 nm and 0.311 nm, respectively. We can corroborate that those values were consistent with their corresponding theoretical inter-planar spacing values from the calculation using 2θ in the XRD patterns. Conversely, there were mixed and smaller nanocrystal domains in ZrO<sub>x</sub>. The FFT pattern of ZrO<sub>x</sub> verified that there were mixed phases comprising tetragonal (112) and monoclinic (111) phases, whose d-spacing values were 0.181 nm and 0.284 nm, respectively. Similar to HfO<sub>x</sub>, these d-spacing values were congruent with their equivalent theoretical inter-planar spacing values obtained from the 2θ computation in Fig. 2f. Subsequently, we can calculate the average nanocrystal size for the corresponding phases using the Scherrer equation[48]. The average grain sizes for representative phases of HfO<sub>x</sub> and ZrO<sub>x</sub> are listed in Table S1. Since the average grain sizes of ZrO<sub>x</sub> are considerably smaller than those of HfO<sub>x</sub>, we can demonstrate that more grain boundaries in ZrO<sub>x</sub> lead to considerable frequency instability owing to a dielectric relaxation. Next, studies on ternary and quaternary multi-component oxide dielectrics will be introduced.

3.3. Electrical and material characterizations of ternary and quaternary oxide films

Before demonstrating the quaternary oxide dielectric, we identified the role of each dielectric component using a ternary oxide system. We extracted the k and J<sub>leak</sub> values from the areal capacitance at a frequency of 1 kHz and J–E curves at 3 MV cm<sup>−1</sup>. Figure 3a illustrates that the k and J<sub>leak</sub> of Al–Hf–O (AHO) increased with increasing HfO<sub>x</sub> content, whereas Fig. 3b reveals that the k and J<sub>leak</sub> of Zr–Al–O (ZAO) decreased as the AlO<sub>x</sub> content increased. Noting that Hf and Zr have lower electronegativities than Al, their incorporation into AlO<sub>x</sub> resulted in a higher dipole moment, leading to a higher k value. However, compared with pure AlO<sub>x</sub>, the ternary oxide exhibited a higher J<sub>leak</sub>. This can be attributed to the relatively low bandgap energies of HfO<sub>x</sub> and ZrO<sub>x</sub>, which can lower the average energy bandgap when blended with AlO<sub>x</sub>[27]. Despite the identical electronegativities of Hf and Zr, the kvalue of Hf–Zr–O (HZO) increased as the Zr content increased (Fig. 3c). From previous crystallographic analyses, we confirmed that the dominant phases of ZrO<sub>x</sub> and HfO<sub>x</sub> were the tetragonal (t) and monoclinic (m) phases, respectively. Notably, the theoretical kvalue for the t-phase of ZrO<sub>x</sub> is higher than that for the m-phase of HfO<sub>x</sub>[49, 50], which accounts for the observed increase in k value with increasing ZrO<sub>x</sub> content.

Consequently, AHZO capacitors were fabricated with various combinatorial composition ratios, and their dielectric parameters were measured. To specify these parameters, color mapping was employed on the triangular phase diagrams (Fig. 3d–f). Each parameter was extracted in the same manner as that for the
ternary oxide-based capacitors. Fig. S3 illustrates triangular phase diagrams for $J_{\text{leak}}$ under different electric fields. This indicates that for $k$ and $E_B$, each parameter follows a continuous monotonic gradient by the contrasting characteristics at each vertex. Both $k$ and $E_B$ decrease monotonically as they approach pure AlO$_x$ and increase as they approach pure ZrO$_x$. As discussed earlier, the binary oxide characteristics support this trend. Moreover, it is observed that AHZO, having lower Al concentration, exhibits an increase in $J_{\text{leak}}$. Insufficient incorporation of AlO$_x$ leads to a narrow bandgap owing to a composition-dependent bandgap distribution; therefore, AHZO is expected to have a smaller conduction band offset with contact metals. Conversely, the Zr–rich ternary and quaternary oxides, demonstrate a strong frequency-dependent capacitance leading to reduced $k$ value at high frequency levels. Fig. S4 presents the triangular phase diagrams for $k$ value extracted at frequencies of 1, 10, and 100 kHz. Upon increasing the frequency level, the high-$k$ regions noted in red close to the HfO$_x$–ZrO$_x$ axis shifted towards the ZrO$_x$ vertex. A comparable phenomenon was also observed near the ZrO$_x$–AlO$_x$ axis, which was regarded as ZrO$_x$–related dielectric relaxation.

Next, we determined the cut-off values for each parameter to screen the optimized stoichiometric ratio of AHZO in the triangular phase diagrams for each dielectric parameter. The regions with $k$ exceeding 11 (purple), $E_B$ exceeding 5 MV cm$^{-1}$ (red), and the order of $J_{\text{leak}}$ below −5.5 (green) are denoted in Fig. 3g. As a result, we were able to select the specific composition ratio of Al:Hf:Zr = 1:2:2, which is highlighted in the triangular phase diagram. To verify the grain-free structural features of the AHZO film, we performed HR-TEM analysis and EDS mapping. Figure 3h illustrates the cross-sectional HR-TEM image of fully amorphous AHZO. Typically, Al-containing ternary oxide dielectrics exhibit an amorphous nature when excess Al (>10 at%) is incorporated into crystalline HfO$_x$ and/or ZrO$_x$.[26] Fig. S5 displays the AFM images of AHZO films with different composition ratios, corroborating the amorphous-derived ultra-smooth surfaces. Furthermore, in the EDS mapping, each component of Al, Hf, and Zr was evenly distributed, suggesting the possibility of securing large-area uniformity.

### 3.4. Electrical characterizations of sub-1.5 V-operated oxide TFTs

Finally, we fabricated a TFT using an AHZO layer with optimal dielectric performance, in which the active layer was a sol-gel IGZO layer. In addition to the dielectric performance, the smooth surface of the dielectric layer is a key factor in realizing high-performance TFTs owing to providing inefficient pathway for charge transport at the channel region, which also deteriorate the reliable operation of TFTs[51].

Based on the AFM results (Fig. S5), the dielectric films exhibited roughness (root-mean-square, RMS) values below 0.2 nm, allowing smooth channel deposition atop the dielectric layer. Figure 4a shows a representative transfer curve of the IGZO/AHZO TFT, with a fixed source-drain voltage ($V_{DS}$) of 1.5 V. Despite the low gate voltage ($V_{GS}$) of 1.5 V, the TFT device exhibited an impressive on/off current ratio ($I_{on}/I_{off}$ ~ $10^6$) and low leakage current ($I_g$ ~ $10^{-10}$ A). This can be attributed to the excellent dielectric properties of the AHZO film. The transfer curves of the IGZO/AHZO TFTs at various stoichiometries are presented in Fig. S6. Figure 4b shows the output curves of the IGZO/AHZO TFT with $V_{GS}$ variation,
demonstrating its cumulative operation. The figure-of-merit parameters of IGZO/AHZO TFTs were obtained by measuring 20 devices to ensure statistical robustness in the measurement. Additionally, Fig. 4c illustrates the statistical Gaussian distribution of the threshold voltage ($V_{TH}$), saturation mobility ($\mu_{sat}$), and subthreshold swing ($SS$). Table S2 summarizes the exact values of the TFTs based on binary oxide dielectrics and AHZO. Although the TFTs based on HfO$_x$ and ZrO$_x$ exhibited considerable $\mu_{sat}$ values owing to their high $k$ values, their crystalline domains inevitably resulted in high $I_{off}$ levels owing to their high $J_{leak}$ levels. In parallel, their $SS$ values, which describe the energy efficiency of TFT as a switch, were relatively higher than those of the AHZO-based TFTs, which could be attributed to surface defects (i.e., grain boundaries) caused by crystallization. Conversely, AlO$_x$-based TFTs are expected to exhibit the lowest $\mu_{sat}$ value compared to AHZO-based TFTs owing to their inferior electric field attenuation capability. Furthermore, TFTs based on other stoichiometric compositions of AHZO exhibited a trend similar to that of binary oxides, resulting in suboptimal figure-of-merit parameters. Consequently, in-depth understanding the stoichiometry of AHZO leads to significantly enhanced figure-of-merit parameters for TFT applications.

Finally, we assessed the reliability of IGZO/AHZO TFTs under bias-stress conditions. Figure 4d and e depict the transfer curve shift after applying constant bias stresses, where $V_{DS}$ was +0.1 V whereas $V_{GS}$ was +1.5 V for positive bias stress (PBS) and −1.5 V for negative bias stress (NBS) tests. Note that typical oxide semiconductors have a large number of free electrons owing to the donor-like oxygen vacancies[52]. Therefore, IGZO, a representative oxide semiconductor, induces an n-channel at the semiconductor–dielectric interface when a positive $V_{GS}$ is applied. A continuous PBS allows steady charge accumulation at the channel region, which electrons can be trapped at the interfaces dielectric layer due to undesired grain boundaries[53]. The electron trapping lead to the decreased $I_{DS}$ at the same voltage, pronounced by a positive shift of $V_{TH}$. On the other hand, NBS causes a negative shift in $V_{TH}$.

Typically, the donor states pinned at the dielectric interfaces provide extra electrons in conduction band of IGZO by NBS-derived band bending, where their energy level is above the Fermi energy level [21]. In the same manner, the bulk trap sites in dielectrics, including point defects and grain boundaries, can release extra electrons to the conduction band of IGZO where their defect level in forbidden gap is above the Fermi energy level of IGZO after NBS-derived band bending[54].

Interestingly, the $V_{TH}$ shifts ($\Delta V_{TH}$) of the IGZO/AHZO TFT under a long-time exertion up to 3600 s were 0.18 V and −0.15 V in PBS (Fig. 4f) and NBS (Fig. 4g), respectively, which were less-shifted rather than IGZO TFTs based on HfO$_x$ (0.26 V for PBS, −0.21 V for NBS) and ZrO$_x$ (0.32 V for PBS, −0.32 V for NBS). As we proposed earlier, the chronic sources for driving bias instability of solution-derived oxide dielectrics are surface and bulk defects. To evaluate the defect distributions, we calculated the interface trap density ($D_{it}$) for the corresponding oxide dielectrics and summarized the results in Table S3. The tabulated results indicate that AHZO exhibit less surface trap sites rather than other high-$k$ dielectrics such as HfO$_x$ and ZrO$_x$. Furthermore, it is also regarded that AHZO has less bulk traps due to its amorphous attributes. On the other hand, the AlO$_x$-based TFTs (0.40 V for PBS, −0.47 V for NBS)
exhibited inferior bias-stability to the AHZO-based TFTs despite its amorphous feature. Upon our hypothesis, this might be attributed to the absence of \( d \)-orbital-assisted orbital hybridization in \( \text{AlO}_x \) or competitively low \( k \) value\[55\], suggesting further investigation later. Consequently, we successfully demonstrated the bias-stress-stable sub-1.5 V TFTs albeit without employing sub-10 nm dielectric layer.

4. Conclusions

In this study, we fabricate bias-stress stable all-solution processed IGZO TFTs operated under 1.5 V via an in-depth and systematic studies on sol-gel quaternary AHZO dielectric film. By comprehending the individual contributions of these binary oxides and performing extensive screening, we were able to tailor the dielectric performance, which was marked by \( k \) exceeding 10, an average \( E_B \) surpassing 5 MV cm\(^{-1}\), and a \( J_{\text{leak}} \) below \( 10^{-5.5} \) A cm\(^{-2}\). Unlike other high-\( k \) multi-component dielectrics, the AHZO film exhibited a pronounced amorphous feature, which guaranteed an exceptionally smooth surface as well as an exclusion of grain boundaries for minimized bulk and interface trap sites. Consequently, a sol-gel-derived IGZO TFT with AHZO dielectric layer exhibited not only enhanced electrical performance at sub-1.5 V gate bias but also improved bias stability under both PBS and NBS conditions with negligible hysteresis loop. We expect that these systematical investigations on multi-component dielectrics will open a new era for advanced TFT technology requiring reliable and energy-efficient device operation.

Declarations

Data availability

Data will be made available on request.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


Figures
Figure 1

a) Facile preparation of combinatorial oxide dielectric films. b) Ternary diagram for precursor solutions of combinatorial Al–Hf–Zr–O (AHZO) with different concentration ratios. c) Schematic of fabrication steps for i) combinatorial AHZO-based capacitors, and subsequent ii) IGZO-based thin-film transistors (TFTs).
Figure 2

Evaluation of dielectric performance and crystalline structures of binary oxide thin films. Leakage current density as function of electric fields and areal capacitance with frequency variation of sol-gel a) AlO$_x$, b) ZrO$_x$, and c) HfO$_x$ MIM capacitors. XRD patterns and high-resolution transmission electron microscopy (HR-TEM) images (scale bars indicate 5 nm) of d), g) AlO$_x$, e), h) ZrO$_x$, and f), i) HfO$_x$ thin films. The inset images denote the fast Fourier transformation (FFT) patterns with colored highlights.
Figure 3

Evaluation of dielectric performance of ternary oxide films. Plots of $E_B$, $k$, and $J_{\text{leak}}$ as functions of partial atomic ratios; a) Al–Hf–O, b) Zr–Al–O, and c) Hf–Zr–O. Phase diagrams for quaternary oxide dielectrics with the figure-of-merit parameters; d) $k$, e) $E_B$, and f) leakage current. g) Cut-off regions for each figure-of-merit parameter colored in purple ($k$), red ($E_B$), and green ($J_{\text{leak}}$). h) Cross-sectional HR-TEM image of combinatorial AHZO film and corresponding energy dispersive spectroscopy (EDS) mapping image, for which the stoichiometry of combinatorial AHZO is 1:2:2. Scale bar in TEM image denotes 5 nm.
Figure 4

Electrical characterizations of IGZO TFTs using combinatorial AHZO film as dielectric layer. Representative a) transfer and b) output curves of IGZO/AHZO TFT. c) Statistical distributions of figure-of-merit parameters of IGZO/AHZO TFTs, including threshold voltage, saturation mobility, and subthreshold swing. Denoted $\mu$ and $\sigma$ indicate the mean and error values, respectively. Reliability tests of IGZO/AHZO TFT under bias stress up to 3600 s; d) PBS ($V_{GS} = +1.5$ V) and e) NBS ($V_{GS} = -1.5$ V), respectively. Time-dependent $V_{TH}$ shifts of IGZO TFTs based on binary oxide and AHZO, under f) PBS and g) NBS conditions.

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