



# Engineering Bilayer $\text{AlO}_x$ / $\text{YAIO}_x$ Dielectric Stacks for Hysteresis-Free Switching in Solution-Processed Metal-Oxide Thin-Film Transistors

Sami Bolat<sup>1\*†</sup>, Evangelos Agiannis<sup>1†</sup>, Shih-Chi Yang<sup>1</sup>, Moritz H. Futscher<sup>1</sup>, Abdesselam Aribia<sup>1</sup>, Ivan Shorubalko<sup>2</sup> and Yaroslav E. Romanyuk<sup>1\*</sup>

<sup>1</sup>Laboratory for Thin Films and Photovoltaics, Empa- Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, <sup>2</sup>Transport at Nanoscale Interfaces Laboratory, Empa- Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

## OPEN ACCESS

### Edited by:

Giovanni Antonio Salvatore,  
Ca' Foscari University of Venice, Italy

### Reviewed by:

Fei Hui,  
Technion Israel Institute of  
Technology, Israel  
Nazek El-Atab,  
King Abdullah University of Science  
and Technology, Saudi Arabia

### \*Correspondence:

Sami Bolat  
sami.bolat@empa.ch  
Yaroslav E. Romanyuk  
Yaroslav.romanyuk@empa.ch

<sup>†</sup>These authors have contributed  
equally to this work

### Specialty section:

This article was submitted to  
Flexible Electronics,  
a section of the journal  
Frontiers in Electronics

Received: 29 October 2021

Accepted: 06 December 2021

Published: 07 January 2022

### Citation:

Bolat S, Agiannis E,  
Yang S-C, Futscher MH, Aribia A,  
Shorubalko I and Romanyuk YE (2022)  
Engineering Bilayer  $\text{AlO}_x$  /  $\text{YAIO}_x$   
Dielectric Stacks for Hysteresis-Free  
Switching in Solution-Processed  
Metal-Oxide Thin-Film Transistors.  
Front. Electron. 2:804474.  
doi: 10.3389/felec.2021.804474

Solution processing and low-temperature annealing ( $T < 300^\circ\text{C}$ ) of the precursor compounds promise low-cost manufacturing for future applications of flexible oxide electronics. However, thermal budget reduction comes at the expense of increased charge trapping residuals in the dielectric layers, which result in hysteretic switching of transistors. This work reports on a novel bilayer dielectric scheme combining aluminum oxide ( $\text{AlO}_x$ ) as a positive charge trapping insulator and yttrium aluminum oxide ( $\text{YAIO}_x$ ) as a negative charge trapping dielectric to obtain hysteresis free switching in the solution-processed metal-oxide thin-film transistors. Devices were processed at a thermal budget of  $250^\circ\text{C}$ , without an encapsulation layer. The presence of  $\text{H}^+$  and  $\text{OH}^-$  in the  $\text{AlO}_x$  were found responsible for the hysteresis in the switching, which was suppressed successfully with the thickness optimization of the  $\text{YAIO}_x$  in the dielectric stack. Fabricated devices yield ON/OFF ratios of  $10^6$ , sub-pA level gate leakage currents, a subthreshold swing of 150 mV/decade, and field-effect mobility of  $1.5 \text{ cm}^2/\text{V}\cdot\text{sec}$ .

**Keywords:** solution processing, metal oxides, dielectrics, low temperature curing, charge trapping, thin-film transistor (TFT)

## INTRODUCTION

The driving element of flexible electronics is the thin-film transistor (TFT), finding applications in flat panel displays (Barquinha et al., 2012), digital and analog circuitries (Petti et al., 2016), and sensors (Smith et al., 2014; Knobelspies et al., 2018). Metal-oxide semiconductors are implemented in the mainstream TFTs for today's display industry, thanks to their intrinsically high motilities ( $\mu \sim 50\text{--}100 \text{ cm}^2/\text{V}\cdot\text{sec}$ ) (Paterson and Anthopoulos, 2018). The sputtering method, commonly employed for depositing metal-oxide semiconductors, offers excellent uniformity over large areas necessary/required for displays. Encapsulated metal-oxide TFTs have several years of lifetime stability, solving the issue of the formerly dominant technology with a-Si-based TFTs (Fortunato et al., 2012). Thanks to the wide band-gap ( $E_G > 3 \text{ eV}$ ) of the semiconductor, ultralow leakage current in the off operation ( $I_{\text{leakage}} < \text{pA}$ ) is obtained from oxide based TFTs.

In the rising era of flexible electronics and optoelectronics, solution-processing methods are investigated as low-cost alternatives to vacuum-based processing (Kim et al., 2014). The ease of manufacturing and availability of inexpensive precursors make solution processing attractive for

researchers. The conventional synthesis route of the materials from precursor solutions to dense metal oxide networks requires thermal treatment at high temperatures ( $T > 400^\circ\text{C}$ ) (Lee et al., 2018). Alternative methods, such as light-assisted annealing (Kim et al., 2012; Bolat et al., 2019; Gilshtein et al., 2020; Mancinelli et al., 2020), microwave annealing (Hwang et al., 2011; Cheong et al., 2015) and solution-combustion synthesis (Kim et al., 2011; Liu et al., 2017) enable lower process temperatures compatible with flexible substrates.

Because of the low-temperature processing, residuals of the forming precursors and solvents can remain in the solution-processed layers (Wang et al., 2018). These residuals can create intrinsic defects in the layers, resulting in unexpected charge trapping/migration under a field effect (Jin et al., 2016). This property, if happens in the dielectric layer, results in hysteretic switching behavior of the TFTs. Depending on the behavior of the defects (or residuals) clockwise (Bolat et al., 2019) or counterclockwise hysteresis (Bolat et al., 2020) can be observed in the transfer characteristics of the device. Counterclockwise hysteresis was reported with various dielectrics cured at low temperatures ( $T < 300^\circ\text{C}$ ) such as  $\text{AlO}_x$  (Liang et al., 2020a),  $\text{GdO}_x$  (Zhou et al., 2020), and  $\text{ZrO}_x$  (Kim et al., 2020). This behavior was usually complemented with unprecedentedly high mobility values compared to vacuum-based counterparts, which were reflected as mA range ON currents in the transistors (Daunis et al., 2018). There have been several hypotheses to explain the underlying mechanism for the high mobility in these devices, such as electron donation from dielectric to channel layer during the device operation (Zeumault and Subramanian, 2016), and or electron migration from the dielectric towards the gate contact (Daunis et al., 2018), gate capacitance dependent mobility behavior (Lee et al., 2014), together with the underestimated dielectric constant in the studies due to the use of a high frequency (>kHz) capacitance value to extract the mobility from static transfer characteristic measurements. Such behavior was closely related to the presence of the water within the dielectric (Daunis et al., 2018). In addition to the electron migration hypothesis, Liang et al. (Liang et al., 2020b) underlined another phenomenon existing in solution-processed  $\text{AlO}_x$  dielectrics. It was observed that at the quasi-static frequencies, in addition to the readily existing high electric double-layer (EDL) capacitance, a bias dependent capacitance was present due to faradaic charge transfer at the interfaces of the dielectric with semiconductor and metal layers, which increased the gate capacitance by almost two orders of magnitude (the so-called pseudo capacitance effect). This effect was held responsible for the increased ON current in the transistors. Consequently, the mobility values of TFT devices had to be revised and were significantly lower than those estimated without considering the pseudo capacitance effect.

Hysteresis-free electrical switching is desired for stable operation of the TFTs in their implementation for flat panel displays and digital circuits (Fortunato et al., 2012; Wager, 2020). One way of minimizing the hysteresis of the bottom gated TFTs in the transfer characteristics is to increase the post-deposition annealing temperature of the solution-processed dielectrics, contradicting the needs of flexible electronics processing or by

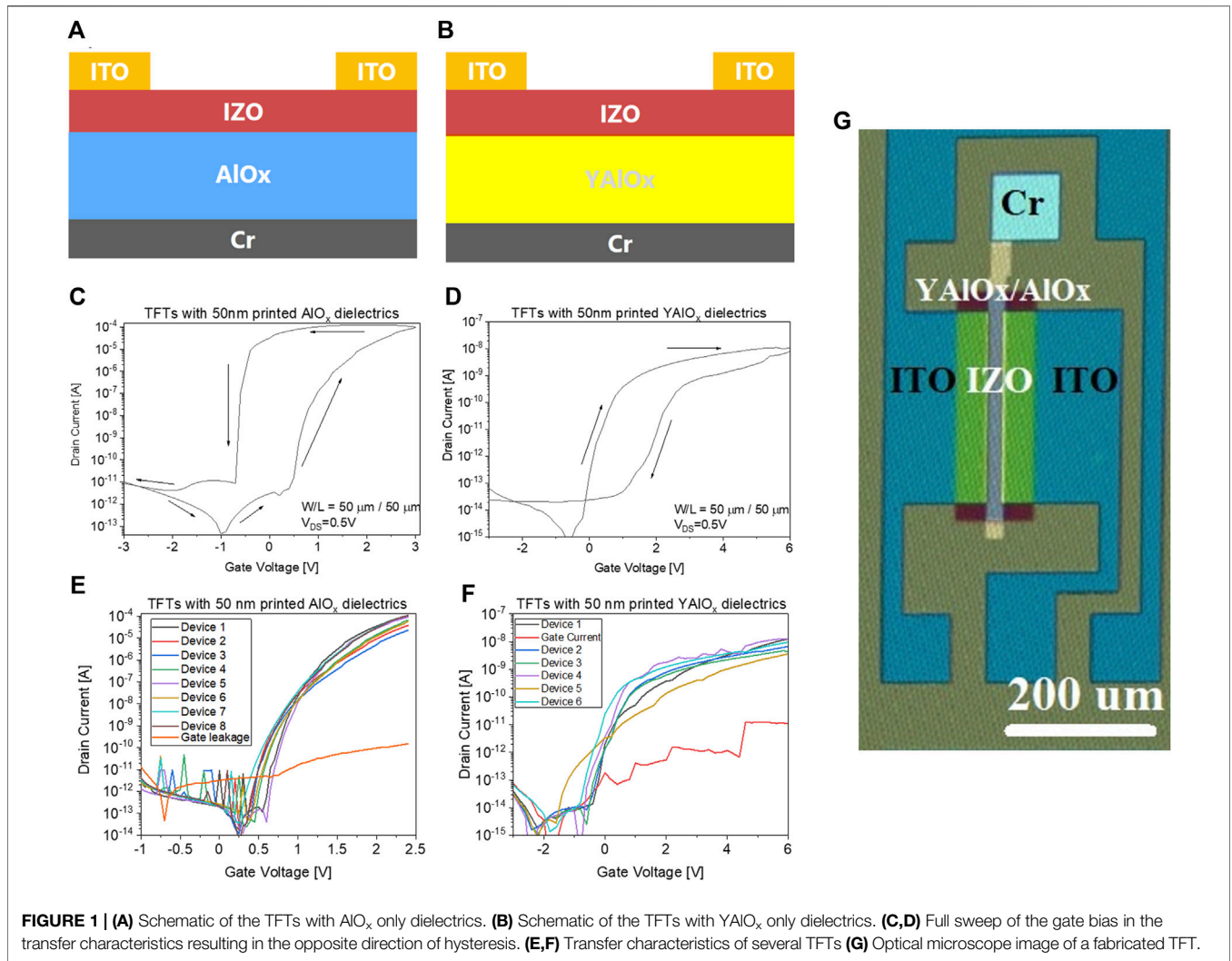
encapsulation of the fabricated devices (Wang et al., 2018). We explore an alternative approach to engineering the dielectric stack using various insulators, with counterbalancing charge-trapping properties, when combined in a TFT offering minimal hysteresis. This approach is advantageous over the former methods, as it does not hinder the properties of the layers processed after the dielectrics. Also, it diminishes the need for the via hole opening of the source-drain contacts, which is required after the encapsulation layer deposition. The flexible TFTs with DUV annealed  $\text{YAlO}_x$  dielectrics (Bolat et al., 2019) included positive shifts in the  $V_T$  due to positive gate bias stress, which is a sign of negative charge trapping within the dielectric. In contrast, the devices with DUV annealed  $\text{AlO}_x$  dielectrics (Bolat et al., 2020) (Mancinelli et al., 2020) had counter clockwise hysteresis in their transfer characteristics as a sign of positive charge trapping in the dielectric layer. In this study tuning the sign and magnitude of the hysteresis in the transfer characteristics of the TFTs is implemented by stacking solution-processed  $\text{AlO}_x$  and  $\text{YAlO}_x$  layers cured with deep ultraviolet assisted annealing at  $250^\circ\text{C}$  as the insulators of the devices. Thicknesses of the layers and their respective position in the devices were optimized to achieve a hysteresis-free operation. Detailed electrical and chemical analyses were performed to shed light on the origin of the charge trapping mechanism.

## RESULTS AND DISCUSSION

Initial experiments were conducted with devices having only one type of dielectric, i.e.,  $\text{AlO}_x$  or  $\text{YAlO}_x$ . Two layers of dielectrics were inkjet printed to ensure pinhole-free deposition (resultant thickness  $\sim 50$  nm). Cross-sectional schematics of the TFTs are shown in **Figures 1A,B**. Full-sweep transfer characteristics of the TFTs are shown in **Figures 1C,D**. Transfer characteristics of the devices with various W/L ratios ( $W/L = 2\text{--}20$ ) are shown in **Figures 1E,F**. A microscope image from the top of a fabricated TFT is given in **Figure 1G**. Device parameters extracted from transfer characteristics are given in **Table 1**.

The devices with  $\text{AlO}_x$  dielectrics have four orders of magnitude higher ON current than their  $\text{YAlO}_x$  employing counterparts. This behavior can be related to the electrolyte behavior of the solution-processed  $\text{AlO}_x$  dielectrics.  $\text{YAlO}_x$  dielectrics have been reported to have minimal to almost no dispersion in their capacitance values at the 0.1 Hz- 1 MHz frequency range (Gillan et al., 2021). The permittivity of  $\text{YAlO}_x$  was extracted as 9.1 in our previous study (Bolat et al., 2019). The permittivity of the printed and low-T ( $250^\circ\text{C}$ ) cured  $\text{AlO}_x$  can be as high as 40 at the quasi-static frequency levels. Still, this would yield only one order of magnitude difference in the ON current by itself. In addition to the electric double-layer capacitance, faradaic charge exchanges at the quasi-static frequency levels (Liang et al., 2020b), reflects as several orders of magnitude increase in the capacitance of the MOS capacitor. This can explain the difference in the ON current of the devices observed here, as well.

The TFTs with  $\text{AlO}_x$  dielectrics suffer from counterclockwise hysteresis (positive charge trapping) in their turn-off transients



**FIGURE 1 | (A)** Schematic of the TFTs with  $\text{AlO}_x$  only dielectrics. **(B)** Schematic of the TFTs with  $\text{YAIO}_x$  only dielectrics. **(C,D)** Full sweep of the gate bias in the transfer characteristics resulting in the opposite direction of hysteresis. **(E,F)** Transfer characteristics of several TFTs **(G)** Optical microscope image of a fabricated TFT.

**TABLE 1 |** Device parameters of the TFTs with a single type of dielectric layers.

Extracted parameter	TFTs with $\text{AlO}_x$ dielectrics	TFTs with $\text{YAIO}_x$ dielectrics
ON current (A)	$10^{-4}$	$10^{-8}$
ON/OFF ratio	$10^8$	$10^5$
Subthreshold swing (mV/decade)	80	200
ON voltage (V)	$0.45 \pm 0.15$	$-0.6 \pm 0.2$
Threshold voltage (V)	1.6	0.35
Gate leakage current at the threshold voltage (A)	$10^{-10}$	$10^{-13}$

(Figure 1C). The full sweep of the transfer characteristics of the  $\text{YAIO}_x$  employing devices instead reveals clockwise hysteresis (Figure 1D). Clockwise hysteresis results from negative charge trapping within the dielectric and/or in the dielectric semiconductor interface (Cross and De Souza, 2006). The trapped negative charges screen the effect of the gate bias, and the accumulated channel region depletes at higher voltages than expected during the turn-off transient. A conclusion on these results is that, on the one hand, the gate stacks employing printed

$\text{AlO}_x$  or  $\text{YAIO}_x$  are not suitable by themselves for hysteresis-free switching applications. Observation of the opposite direction of hysteresis (countersign charge trapping), on the other hand, ignites the idea of implementing a bilayer scheme, which can minimize the hysteretic behavior in the switching after the thicknesses are optimized. To prove the hypothesis, TFTs with bilayer  $\text{AlO}_x/\text{YAIO}_x$  dielectric stack were manufactured *via* spin coating of the metal-oxide layers and following the fabrication as mentioned in the experimental section for device manufacturing.

**TABLE 2** | Thicknesses of the  $\text{AlO}_x/\text{YAIO}_x$  bilayer dielectrics.

$\text{AlO}_x/\text{YAIO}_x$	Thickness (nm)	n
4 layers/0 layer	28.8	1.564
3 layers/1 layer	29.2	1.595
2 layers/2 layers	29.9	1.606
1 layer/3 layers	30.0	1.602
0 layer/4 layers	30.8	1.604

The total thickness of the dielectric layer stack was reduced to ~30 nm to provide better gate control and reduce the operating voltage of the devices. Ellipsometry measurements were performed to determine the thickness of the layers. **Table 2** shows the extracted refractive index from the dielectric stacks along with the measured thickness. A Cauchy model was used for fitting the data.

The thicknesses of the layers are in the  $\sim 30 \pm 1$  nm range, with the refractive index increasing in line with the amount of  $\text{YAIO}_x$  in the stack.  $\text{Y}_2\text{O}_3$  has a higher refractive index than  $\text{Al}_2\text{O}_3$ , which supports the observed behavior.

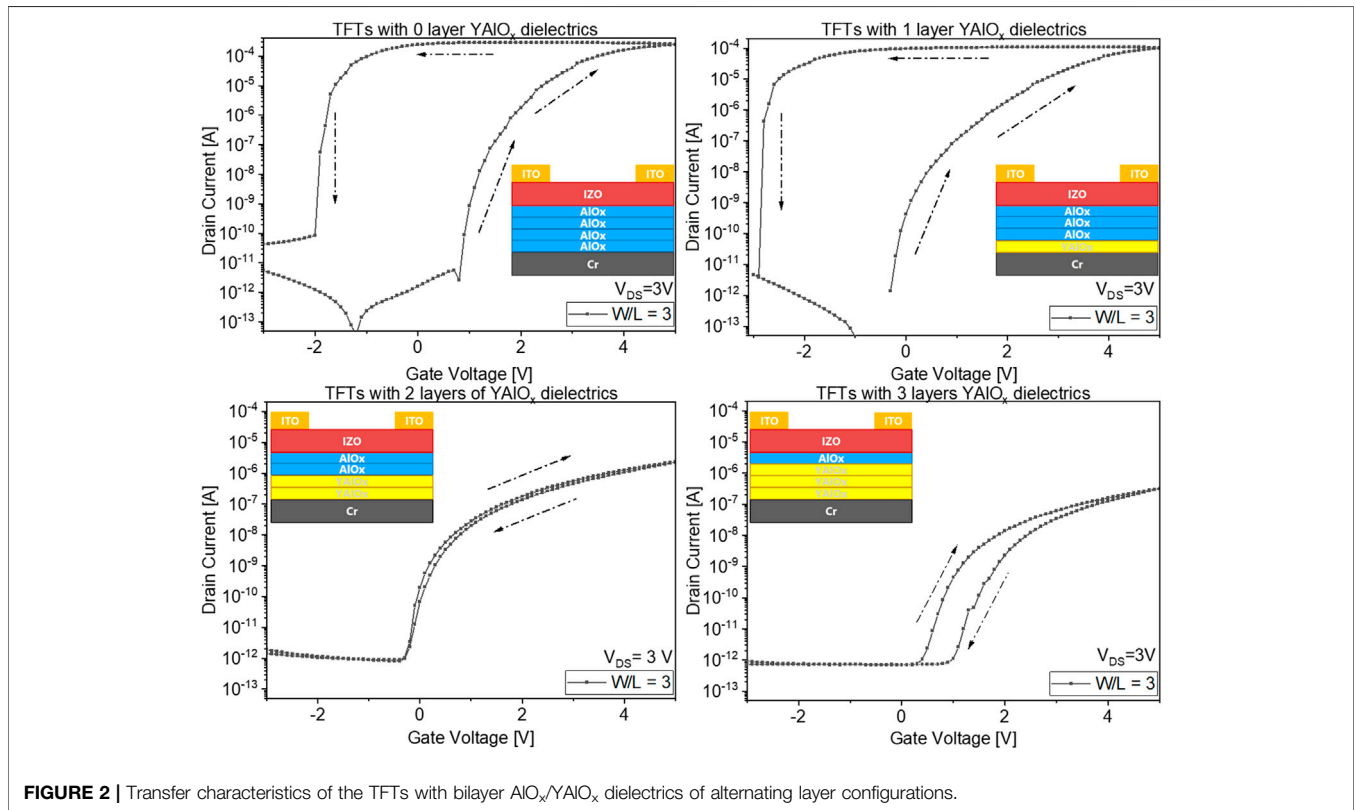
Dielectric stacks with the configurations shown in **Table 2** are later implemented in bottom gated TFTs. As the TFTs with  $\text{AlO}_x$  only case and initial experiments with bilayer scheme yielded higher ON currents with  $\text{AlO}_x$  in contact with the channel layer (**Figure 1A**; **Supplementary Figure S1**), the  $\text{AlO}_x$  layer was used as the uppermost layer in contact with the semiconducting IZO

channel in these experiments, too. Electrical characterizations were performed on the TFTs to investigate the hysteretic behavior. Transfer characteristics of the devices are shown in **Figure 2**. For an easy understanding, the samples were given the names according to the number of  $\text{YAIO}_x$  layers inside, i.e., 0 layer  $\text{YAIO}_x$ , 1 layer  $\text{YAIO}_x$ , 2 layers  $\text{YAIO}_x$ , and 3 layers  $\text{YAIO}_x$ .

Obtained characteristics reveal that the counterclockwise hysteresis is present for the 0 layers  $\text{YAIO}_x$  and 1-layer  $\text{YAIO}_x$  dielectrics cases. Devices with 2 layers of  $\text{YAIO}_x$  dielectrics show minimal hysteresis, whereas the 3 layers  $\text{YAIO}_x$  employing devices have clockwise hysteresis in their transfer characteristics. From these results, one can conclude that by alternating the layer thicknesses in the insulator stack, it is possible to obtain hysteresis-free switching in the bottom gated solution-processed oxide TFTs, even without an encapsulation layer. **Table 3** shows the device parameters extracted from the transfer characteristics.

C-V characteristics were obtained from MOS capacitors with  $100 \mu\text{m} \times 100 \mu\text{m}$  areas at various frequencies to understand the device operation better. **Figure 2A** shows the frequency dispersion of the dielectric constant for the bilayer dielectrics. **Figure 2B** shows the measurement results at 10 Hz, the lowest measurement frequency, which is later, used to minimize the overestimation in the extracted mobility of the devices.

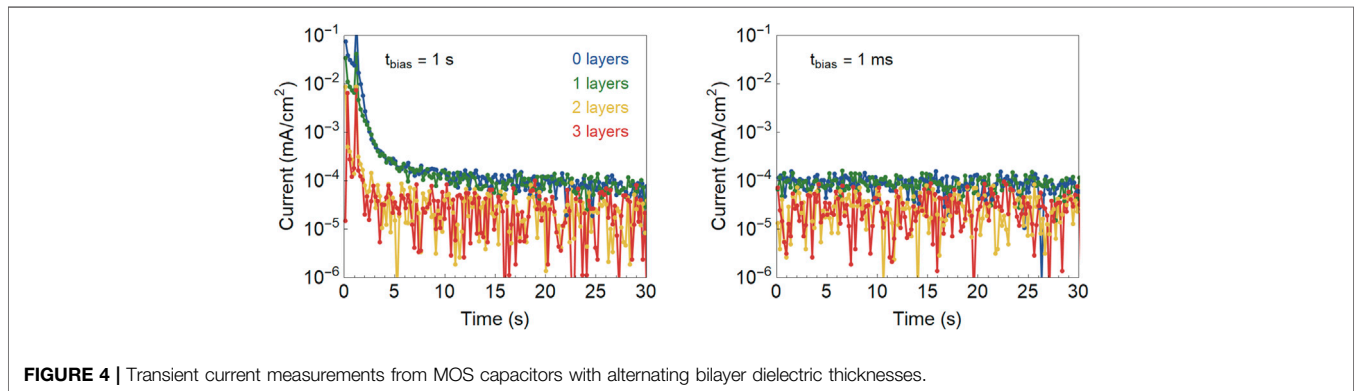
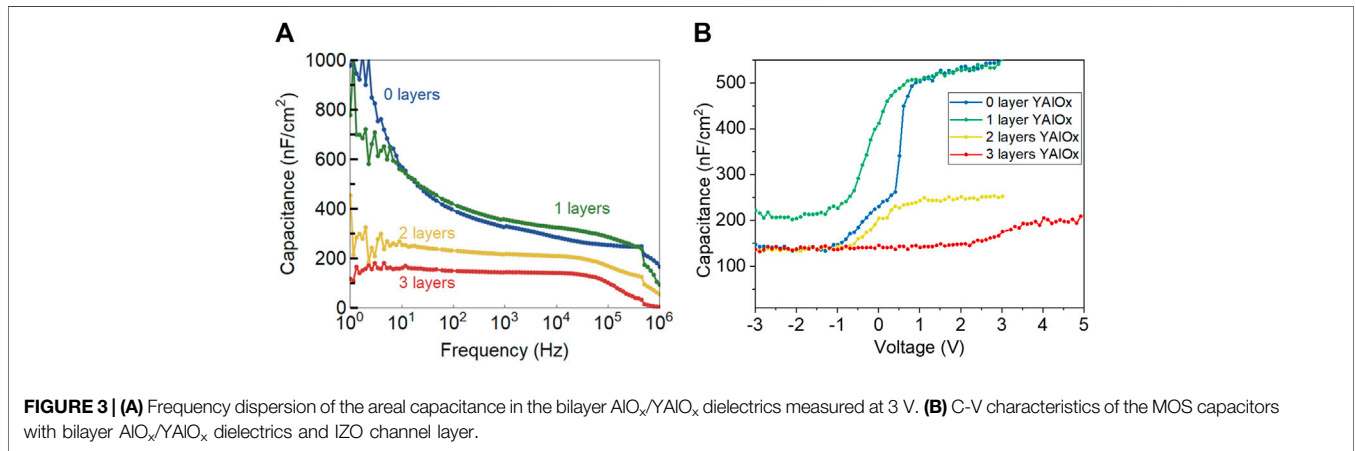
Electrolyte behavior supported by the low-frequency dispersion of capacitance is diminished with the insertion of 2 layers (~15 nm  $\text{YAIO}_x$ ) dielectric into the insulator stack.



**FIGURE 2** | Transfer characteristics of the TFTs with bilayer  $\text{AlO}_x/\text{YAIO}_x$  dielectrics of alternating layer configurations.

**TABLE 3** | Device parameters of the TFTs with bilayer dielectric layers.

Extracted parameter	0 layer YAlO <sub>x</sub>	1 layer YAlO <sub>x</sub>	2 layers YAlO <sub>x</sub>	3 layers YAlO <sub>x</sub>
ON current (A)	$3 \times 10^{-4}$	$2 \times 10^{-4}$	$3 \times 10^{-6}$	$5 \times 10^{-7}$
ON/OFF ratio	$10^8$	$10^8$	$10^6$	$10^5$
Subthreshold swing (mV/decade)	80	100	150	300
ON voltage (V)	0.45 V	-0.6	-0.15	0.20
Threshold voltage (V)	1.6 V	1 V	1.2 V	1.8 V
Gate leakage current at threshold voltage (A)	$10^{-10}$	$10^{-11}$	$<10^{-12}$	$<10^{-12}$



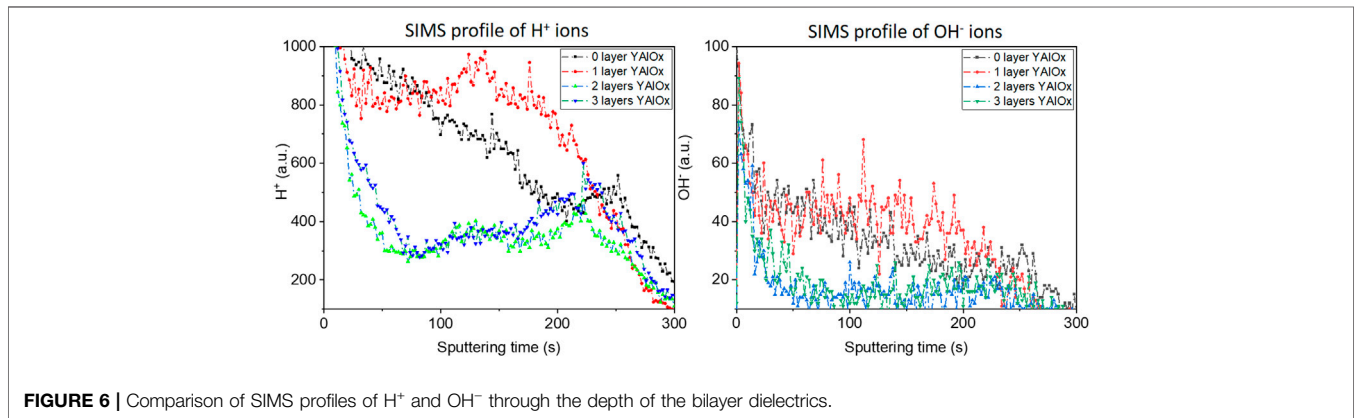
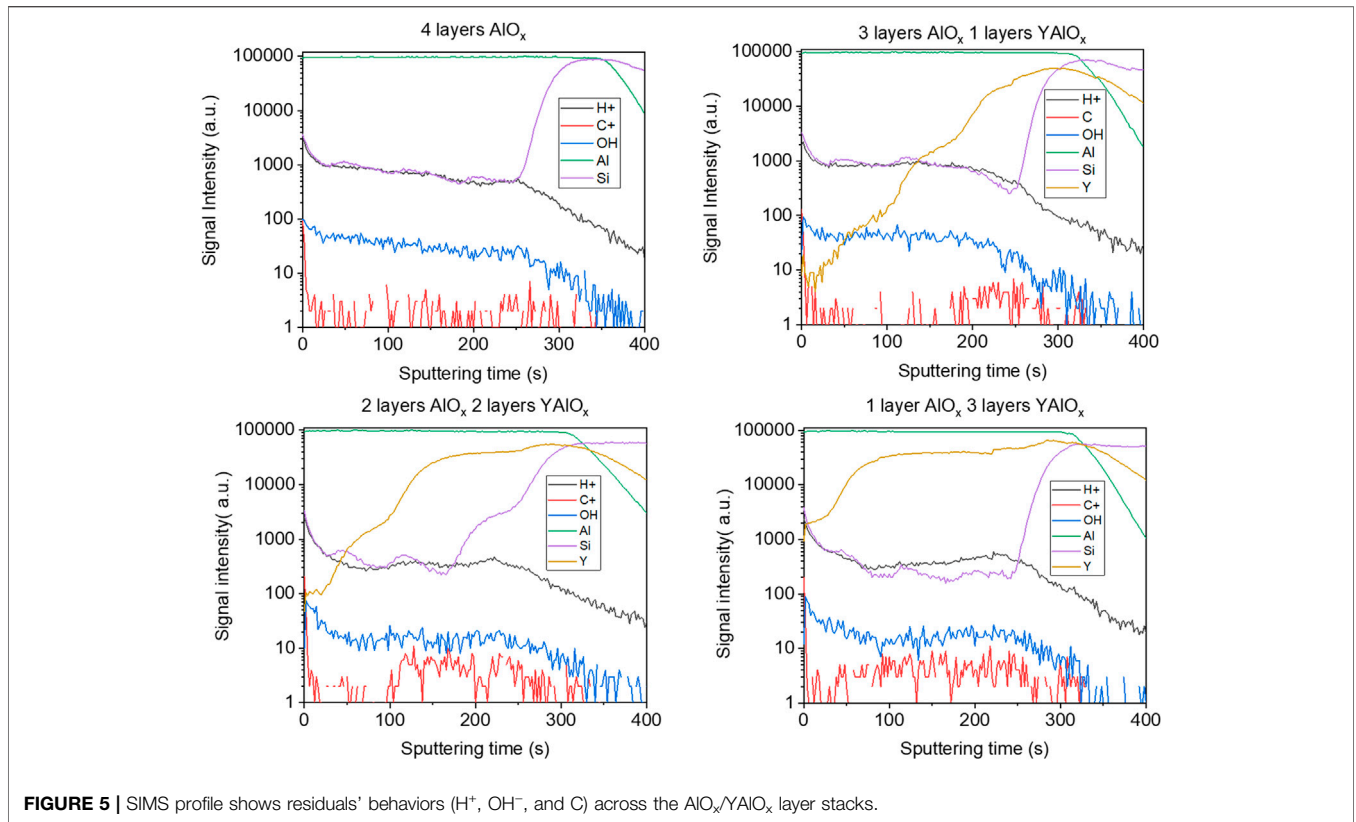
Transient current analyses were performed on the MOS capacitors to estimate a time-dependent behavior for the effective charge trapping in the structures. Pulses of 3 V were applied to the gate for two different periods, while the semiconductor contact was kept at ground level. Finally, the resulting transient current was measured at a gate bias of -3 V. Figure 3 shows the obtained results.

Since long filling times (~seconds range) are required to observe transients, the measured signals can be assigned to ionic rather than electronic defects, since electronic defects should already be visible at a filling time of 1 ms, but not ionic defects. (Futscher et al., 2020). Residuals in the AlO<sub>x</sub> dielectrics, such as H<sup>+</sup> and OH<sup>-</sup> ions, were reported partly responsible for the enhanced quasi-static frequency

polarization in the dielectric (Daunis et al., 2018; Bolat et al., 2020; Liang et al., 2020b). Secondary ion mass spectroscopy (SIMS) measurements were performed on the bilayer dielectrics spin-coated on Si wafers to investigate the hypothesis in detail. OH<sup>-</sup> and H<sup>+</sup> and C signals were measured across the dielectric stack, and the results are demonstrated in Figure 4.

H<sup>+</sup> signal level is higher in the 4 layers AlO<sub>x</sub> and 1 layer YAlO<sub>x</sub> samples compared to the samples with thicker YAlO<sub>x</sub> layers. C signal is at the detection noise level in all the layers. A closer look at the H<sup>+</sup> and OH<sup>-</sup> signals from the layers is provided in Figure 5.

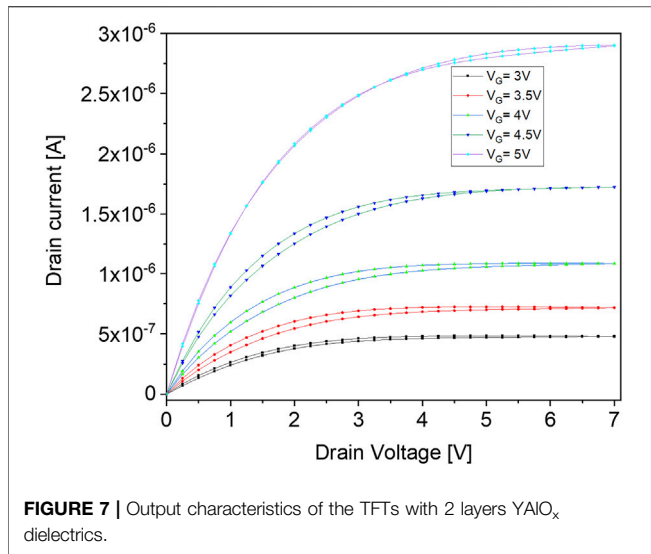
H<sup>+</sup> and OH<sup>-</sup> signals have significantly higher levels for the AlO<sub>x</sub> and 1 layer YAlO<sub>x</sub> samples, supporting the positive charge trapping in the dielectric due to ion movement and charge



exchange in the vicinity of the gate-dielectric interface. The  $H^+$  and  $OH^-$  signal suppresses at the onset of  $YAlO_x$  layer in the samples with thicker  $YAlO_x$  layers (blue and green curves), which can explain the decrease of the dielectric constant at the low-frequency regime. As the  $OH^-$  and  $H^+$  ion movement towards the bottom of the dielectric is blocked, the ionic charge movement and charge exchange between gate and dielectric diminishes, which suppresses the electric double-layer capacitance.

For an ease of understanding, we explain the charge trapping, ion migration and suppression of such migration mechanism in the bilayer dielectrics as follows:

Under the field effect of the gate bias, the water molecules in the  $AlO_x$  dielectric dissociate into  $H^+$  and  $OH^-$  ions.  $H^+$  and  $OH^-$  ions move towards the semiconductor and gate contacts, respectively. This results in the electric double layer formation at the interfaces as also reported in previous works (Yuan et al., 2010; Dausis et al., 2018; Liang et al., 2020b). Existence of the  $H^+$  ions at the oxide semiconductor interface further enhances the field effect by orders of magnitude due to the faradaic charge exchange between the adsorbed  $H^+$  ions and semiconductor, resulting in the pseudocapacitance. This process can be considered as protonation of the semiconductor dielectric interface and was



also reported by Yuan et al. for a H<sub>2</sub>O doped electrolyte ZnO interface (Yuan et al., 2010). Since the dehydrogenation requires a large energy, channel stays ON until a large negative bias is applied from the gate contact (Figure 6). For the devices with YAIO<sub>x</sub> dielectrics, the ion movement blocking takes effect for the scenarios where the YAIO<sub>x</sub> thickness is more than 10 nm. For the single layer case (1 layer YAIO<sub>x</sub>), the H<sup>+</sup> and OH<sup>-</sup> ions are not suppressed and can reach until the gate, as confirmed by SIMS measurements (Figure 5). For the bilayer dielectric containing stacks with YAIO<sub>x</sub> thickness >10 nm, use of AlO<sub>x</sub> at the insulator semiconductor interface results in a higher ON current than the devices where YAIO<sub>x</sub> is placed in contact with the semiconducting channel layer, despite using identical thicknesses for each material. This can be seen in Supplementary Figure S1 and be related to the hydrogen rich nature of the AlO<sub>x</sub> resulting in the electron donation to the channel, as reported by Daunis et al. and also by Zermault and Subramanian. (Zermault and Subramanian, 2016; Daunis et al., 2018).

Devices with two layers YAIO<sub>x</sub> dielectrics were characterized electrically to obtain their output characteristics since the minimal hysteresis was obtained for this dielectric configuration. Results are shown in Figure 7. μ<sub>FE</sub> is extracted from the output characteristics at a drain voltage of 3 V in the saturation region using Eq. 1 as ~1.5 cm<sup>2</sup>/V.sec.

$$\mu_{FE} = \frac{2L}{WC_{Ox}} \left( \frac{d\sqrt{I_{DS}}}{dV_{GS}} \right)^2 \quad (1)$$

It is important to consider that the mobility is not affected only by the dielectric itself, the low temperature processing also results in high amount of hydroxides in the semiconducting layers, thereby reducing the mobility of the devices. Daunis et al. also reported reduction of the extracted mobility with the insertion of ion blocking dielectric layer into the gate stack, where they observed a reduction from 117 cm<sup>2</sup>/V.sec to 4.6 cm<sup>2</sup>/V.sec after the suppression of the hysteretic behavior (Daunis et al., 2018).

## CONCLUSION

Solution processing promises low-cost manufacturing of oxide electronics on flexible substrates. This requires temperature reduction of the post deposition annealing of the as-deposited precursors, which results in anomalous charge trapping in the dielectric layers. In this work, the effects of implementing two counterbalancing charge-trapping dielectrics (YAIO<sub>x</sub> and AlO<sub>x</sub>) in low-temperature cured solution-processed TFTs were investigated. Increasing the thickness of the negative charge trapping YAIO<sub>x</sub> in the bilayer dielectric stack was observed to diminish the EDL capacitance thought to be originated from H<sup>+</sup> and OH<sup>-</sup> ion migration in the AlO<sub>x</sub> dielectrics. Detailed SIMS analysis revealed the significant decrease of the H<sup>+</sup> and OH<sup>-</sup> ions in the YAIO<sub>x</sub> dielectrics, supporting the hypothesis. A stack of 15 nm YAIO<sub>x</sub> 15 nm AlO<sub>x</sub> offered hysteresis-free transistor switching, providing an alternative methodology to obtain stable operation. This methodology can be extended to various insulators with counterbalancing charge trapping and provide a general manufacturing route for high-performance, stable switching low-temperature solution-processed oxide transistors.

## EXPERIMENTAL

**Ink preparation:** YAIO<sub>x</sub> (Y: Al, 2:8) and AlO<sub>x</sub> inks were prepared by dissolving Al(NO<sub>3</sub>)<sub>3</sub> × 9H<sub>2</sub>O and Y(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O salts in 50%/50% volume 2-Methoxyethanol/Ethylene glycol. Nominal metal ion concentration was adjusted as 0.4 M for printed dielectrics and 0.1 M for spin-coated layers. Solutions were stirred at 70°C for 12 h and filtered with a 0.2 μm PFTE filter. The viscosity of the printing ink was measured at 25°C by a strain-controlled rheometer (Anton-Paar MCR 301) with plate/plate geometry (25 mm diameter, 0.1 mm gap). It was obtained as 12 cP falling in a suitable range for inkjet printing.

**IZO ink** was prepared by dissolving In(NO<sub>3</sub>)<sub>3</sub> · xH<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O with a total metal ion concentration of 0.2 M (In: Zn, 7:3) in 2-Methoxyethanol. The nominal metal ratio was chosen according to the reported literature (Mancinelli et al., 2020). The solution was stirred at 60°C for 12 h and filtered with a 0.2 μm PFTE filter before deposition.

**TFT fabrication:** A test-grade silicon wafer serving as the substrate was sonicated in acetone (5 min), isopropanol (5 min), and DI water (5 min). Cleaned substrates underwent a buffered oxide etchant exposure to remove the native oxide from the wafers. 100 nm thick SiN<sub>x</sub> was deposited via plasma-enhanced chemical vapor deposition at 150°C to isolate the devices from the substrate. E-beam evaporated Cr (35 nm) was used as gate contact and patterned via photolithography. Dielectric layers were deposited as follows:

**Printed AlO<sub>x</sub> and YAIO<sub>x</sub> dielectrics:** AlO<sub>x</sub> and YAIO<sub>x</sub> were inkjet printed with a resolution of 400 drops-per-inch via LP50 inkjet printer with Dimatix cartridges of 10 pL nozzle volume. Two layers of dielectric ink were printed to avoid pinholes in the insulator.

Printed layers were dried at 250°C, and were exposed to DUV with N<sub>2</sub> flow (6 L/min) for 30 min. DUV annealing is performed with a low-pressure mercury lamp (Filgen Inc. UV253H) with two emission peaks at 184 and 253 nm and output power density of 25–28 mW/cm<sup>2</sup>. Final annealing at 250°C (60 min) in air ambient was applied to densify the cured layers further.

Spin-coated AlO<sub>x</sub> and YAlO<sub>x</sub> dielectrics: 4 layers of dielectrics layers were created by spin-coating at a speed of 4,000 rpm and subsequent drying at 150°C for 5 min. Before every spin-coating, the substrates were exposed to 1 min of oxygen plasma to enhance the wetting of the subsequent layers. Dried layers were exposed to DUV with N<sub>2</sub> flow (6 L/min) for 30 min and later annealed in air at 250°C for 30 min.

Spin-coated IZO channel layer: Two consecutive layers of IZO ink were spin-coated with a speed of 2000 rpm for 30 s and dried at 150°C. The dried semiconductor layer underwent the DUV exposure in the air for 30 min and the last annealing step at 250°C for 60 min. 30 nm thick semiconductor channel was photolithographically patterned and etched with a 1:121 diluted hydrochloric acid solution.

Sputtered ITO contacts: Source and drain contacts were realized via sputtering and lift-off of ITO layers with the following parameters: Sputtering pressure: 0.4 Pa, O<sub>2</sub> Flow: 0 sccm, Ar Flow: 60 sccm, RF sputtering power: 180 W, deposition temperature: room temperature, the thickness of the layer ~100 nm. The sheet resistance of the layer was ~25 ohms/square.

Electrical characterizations: DC characteristics of the TFTs were acquired in the dark with a Keithley 4,200 Semiconductor parameter analyzer. C-V, C-f, and transient measurements on MOS capacitors were performed by using Paios from Fluxim AG. C-V and C-f measurements were performed using an AC voltage of 50 mV.

SIMS measurements: The primary beam was 25 keV Bi<sup>+</sup> ions with a total current of 1.1 pA and a raster size of 50 × 50 μm<sup>2</sup>. For detection of negative ions, Cs<sup>+</sup> ions were used with 500 eV ion energy, 30 nA pulse current on a 300 × 300 μm<sup>2</sup> raster size to bombard and etch the film.

Optical characterizations: Optical characterization and thickness measurement of the AlO<sub>x</sub>/YAlO<sub>x</sub> bilayer dielectrics deposited on Si(<100>) was acquired by ellipsometry (J.A. Woollam M-2000V). The bilayer was modelled as a Bruggeman effective medium approximation (EMA) layer. The fitting was performed using the CompleteEASE software by J.A. Woollam Co.

## REFERENCES

- Barquinha, P., Martins, R., Pereira, L., and Fortunato, E. (2012). *Transparent Oxide Electronics*. Chichester, UK: John Wiley & Sons. doi:10.1002/9781119966999
- Bolat, S., Fuchs, P., Knobelspies, S., Temel, O., Sevilla, G. T., Gilshtein, E., et al. (2019). Inkjet-Printed and Deep-UV-Annealed YAlO<sub>x</sub> Dielectrics for High-Performance IGZO Thin-Film Transistors on Flexible Substrates. *Adv. Electron. Mater.* 5, 1800843. doi:10.1002/aelm.201800843
- Bolat, S., Torres Sevilla, G., Mancinelli, A., Gilshtein, E., Sastre, J., Cabas Vidani, A., et al. (2020). Synaptic Transistors with Aluminum Oxide Dielectrics Enabling Full Audio Frequency Range Signal Processing. *Sci. Rep.* 10, 16664. doi:10.1038/s41598-020-73705-w

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

## AUTHOR CONTRIBUTIONS

SB and YR conceptualized the idea. SB fabricated the devices. EA performed the electrical characterizations on the TFTs with bilayer AlO<sub>x</sub>/YAlO<sub>x</sub> dielectrics, critically analyzed the obtained results, and discussed them with SB, YR, EA, SB, and MF performed the C-f, C-V, and transient current measurements on the MOS capacitors. IS supervised the electrical characterizations. S-CY optimized the sputtering recipe for the ITO contacts and performed the SIMS characterization and analysis on the bilayer dielectrics. AA performed ellipsometry measurements and fitted the obtained results for thickness and optical constant extractions of the layers. YR supervised the study. SB and YR wrote the manuscript with the inputs from all the coauthors. SB and EA contributed equally to this work.

## FUNDING

MHF is supported by a Rubicon Fellowship from the Netherlands Organisation for Scientific Research (NWO).

## ACKNOWLEDGMENTS

Authors acknowledge the financial support from the Strategic Focus Area Advanced Manufacturing of the ETH domain under the project FOXIP - Functional OXides Printed on Polymers and Paper.

## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/felec.2021.804474/full#supplementary-material>

- Cheong, H., Ogura, S., Ushijima, H., Yoshida, M., Fukuda, N., and Uemura, S. (2015). Rapid Preparation of Solution-Processed InGaZnO Thin Films by Microwave Annealing and Photoirradiation. *AIP Adv.* 5, 067127. doi:10.1063/1.4922512
- Cross, R. B. M., and De Souza, M. M. (2006). Investigating the Stability of Zinc Oxide Thin Film Transistors. *Appl. Phys. Lett.* 89, 263513. doi:10.1063/1.2425020
- Daunis, T. B., Tran, J. M. H., and Hsu, J. W. P. (2018). Effects of Environmental Water Absorption by Solution-Deposited Al<sub>2</sub>O<sub>3</sub> Gate Dielectrics on Thin Film Transistor Performance and Mobility. *ACS Appl. Mater. Inter.* 10, 39435–39440. doi:10.1021/acsami.8b15592
- Fortunato, E., Barquinha, P., and Martins, R. (2012). Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances. *Adv. Mater.* 24, 2945–2986. doi:10.1002/adma.201103228



- Futscher, M. H., Gangishetty, M. K., Congreve, D. N., and Ehrler, B. (2020). Quantifying mobile Ions and Electronic Defects in Perovskite-Based Devices with Temperature-dependent Capacitance Measurements: Frequency vs Time Domain. *J. Chem. Phys.* 152, 044202. doi:10.1063/1.5132754
- Gillan, L., Li, S., Lahtinen, J., Chang, C. H., Alastalo, A., and Leppäniemi, J. (2021). Inkjet-Printed Ternary Oxide Dielectric and Doped Interface Layer for Metal-Oxide Thin-Film Transistors with Low Voltage Operation. *Adv. Mater. Inter.* 8, 2100728. doi:10.1002/admi.202100728
- Gilshstein, E., Bolat, S., Sevilla, G. T., Cabas-Vidani, A., Clemens, F., Graule, T., et al. (2020). Inkjet-Printed Conductive ITO Patterns for Transparent Security Systems. *Adv. Mater. Technol.*, 2000369. doi:10.1002/admt.202000369
- Hwang, M.-s., Jeong, B.-y., Moon, J., Chun, S.-K., and Kim, J. (2011). Inkjet-printing of Indium Tin Oxide (ITO) Films for Transparent Conducting Electrodes. *Mater. Sci. Eng. B* 176, 1128–1131. doi:10.1016/j.mseb.2011.05.053
- Jin, J. W., Nathan, A., Barquinha, P., Pereira, L., Fortunato, E., Martins, R., et al. (2016). Interpreting Anomalies Observed in Oxide Semiconductor TFTs under Negative and Positive Bias Stress. *AIP Adv.* 6, 085321. doi:10.1063/1.4962151
- Kim, M.-G., Kanatzidis, M. G., Facchetti, A., and Marks, T. J. (2011). Low-temperature Fabrication of High-Performance Metal Oxide Thin-Film Electronics via Combustion Processing. *Nat. Mater.* 10, 382–388. doi:10.1038/nmat3011
- Kim, S. J., Yoon, S., and Kim, H. J. (2014). Review of Solution-Processed Oxide Thin-Film Transistors. *Jpn. J. Appl. Phys.* 53, 02BA02. doi:10.7567/JJAP.53.02BA02
- Kim, Y.-H., Heo, J.-S., Kim, T.-H., Park, S., Yoon, M.-H., Kim, J., et al. (2012). Flexible Metal-Oxide Devices Made by Room-Temperature Photochemical Activation of Sol-Gel Films. *Nature* 489, 128–132. doi:10.1038/nature11434
- Kim, Y. G., Lv, D., Huang, J., Bukke, R. N., Chen, H., and Jang, J. (2020). Artificial Indium-Tin-Oxide Synaptic Transistor by Inkjet Printing Using Solution-Processed ZrO<sub>2</sub> X Gate Dielectric. *Phys. Status Solidi A* 217, 2000314. doi:10.1002/pssa.202000314
- Knobelspies, S., Bierer, B., Daus, A., Takabayashi, A., Salvatore, G., Cantarella, G., et al. (2018). Photo-Induced Room-Temperature Gas Sensing with A-IGZO Based Thin-Film Transistors Fabricated on Flexible Plastic Foil. *Sensors* 18, 358. doi:10.3390/s18020358
- Lee, E., Ko, J., Lim, K.-H., Kim, K., Park, S. Y., Myoung, J. M., et al. (2014). Gate Capacitance-dependent Field-Effect Mobility in Solution-Processed Oxide Semiconductor Thin-Film Transistors. *Adv. Funct. Mater.* 24, 4689–4697. doi:10.1002/adfm.201400588
- Lee, J., Seul, H., and Jeong, J. K. (2018). Solution-processed Ternary alloy Aluminum Yttrium Oxide Dielectric for High Performance Indium Zinc Oxide Thin-Film Transistors. *J. Alloys Compounds* 741, 1021–1029. doi:10.1016/j.jallcom.2018.01.249
- Liang, X., Li, Z., Liu, L., Chen, S., Wang, X., and Pei, Y. (2020a). Artificial Synaptic Transistor with Solution Processed InOx Channel and AlOx Solid Electrolyte Gate. *Appl. Phys. Lett.* 116, 012102. doi:10.1063/1.5120069
- Liang, X., Liu, L., Cai, G., Yang, P., Pei, Y., and Liu, C. (2020b). Evidence for Pseudocapacitance and Faradaic Charge Transfer in High-Mobility Thin-Film Transistors with Solution-Processed Oxide Dielectrics. *J. Phys. Chem. Lett.* 11, 2765–2771. doi:10.1021/acs.jpcllett.0c00583
- Liu, A., Zhu, H., Guo, Z., Meng, Y., Liu, G., Fortunato, E., et al. (2017). Solution Combustion Synthesis: Low-Temperature Processing for P-type Cu:NiO Thin Films for Transparent Electronics. *Adv. Mater.* 29, 1701599. doi:10.1002/adma.201701599
- Mancinelli, A., Bolat, S., Kim, J., Romanyuk, Y. E., and Briand, D. (2020). Deep-UV-Enhanced Approach for Low-Temperature Solution Processing of IZO Transistors with High-K AlOx/YAlOx Dielectric. *ACS Appl. Electron. Mater.* 2, 3141–3151. doi:10.1021/acsaem.0c00444
- Paterson, A. F., and Anthopoulos, T. D. (2018). Enabling Thin-Film Transistor Technologies and the Device Metrics that Matter. *Nat. Commun.* 9, 5264. doi:10.1038/s41467-018-07424-2
- Petti, L., Münzenrieder, N., Vogt, C., Faber, H., Büthe, L., Cantarella, G., et al. (2016). Metal Oxide Semiconductor Thin-Film Transistors for Flexible Electronics. *Appl. Phys. Rev.* 3, 021303. doi:10.1063/1.4953034
- Smith, J. T., Shah, S. S., Goryll, M., Stowell, J. R., and Allee, D. R. (2014). Flexible ISFET Biosensor Using IGZO Metal Oxide TFTs and an ITO Sensing Layer. *IEEE Sensors J.* 14, 937–938. doi:10.1109/JSEN.2013.2295057
- Wager, J. F. (2020)1975). TFT Technology: Advancements and Opportunities for Improvement. *Inf. Display* 36, 9–13. doi:10.1002/msid.1098
- Wang, B., Huang, W., Chi, L., Al-Hashimi, M., Marks, T. J., and Facchetti, A. (2018). High-k Gate Dielectrics for Emerging Flexible and Stretchable Electronics. *Chem. Rev.* 118, 5690–5754. doi:10.1021/acs.chemrev.8b00045
- Yuan, H., Shimotani, H., Tsukazaki, A., Ohtomo, A., Kawasaki, M., and Iwasa, Y. (2010). Hydrogenation-Induced Surface Polarity Recognition and Proton Memory Behavior at Protic-Ionic-Liquid/Oxide Electric-Double-Layer Interfaces. *J. Am. Chem. Soc.* 132, 6672–6678. doi:10.1021/ja909110s
- Zeumault, A., and Subramanian, V. (2016). Mobility Enhancement in Solution-Processed Transparent Conductive Oxide TFTs Due to Electron Donation from Traps in High-kGate Dielectrics. *Adv. Funct. Mater.* 26, 955–963. doi:10.1002/adfm.201503940
- Zhou, Y., Li, J., Yang, Y., Chen, Q., and Zhang, J. (2020). Artificial Synapse Emulated through Fully Aqueous Solution-Processed Low-Voltage In<sub>2</sub>O<sub>3</sub> Thin-Film Transistor with Gd<sub>2</sub>O<sub>3</sub> Solid Electrolyte. *ACS Appl. Mater. Inter.* 12, 980–988. doi:10.1021/acsmi.9b14456

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

**Publisher's Note:** All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2022 Bolat, Agiannis, Yang, Futscher, Aribia, Shorubalko and Romanyuk. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.