Low-Voltage Heterojunction Metal Oxide Transistors via Rapid Photonic Processing

*Emre Yarali, Hendrik Faber, Emre Yengel, Akmaral Seitkhan, Kalaivanan Loganathan, George T. Harrison, Begimai Adilbekova, Yuanbao Lin, Chun Ma, Yuliar Firdaus, Thomas D. Anthopoulos**

E. Yarali, Dr. H. Faber, Dr. E. Yengel, A. Seitkhan, K. Loganathan, A. Seitkhan, Dr. G. T. Harrison, B. Adilbekova, Y. Lin, C. Ma, Dr. Y. Firdaus, Prof. T. D. Anthopoulos
King Abdullah University of Science and Technology (KAUST),
KAUST Solar Center (KSC), Thuwal 23955, Saudi Arabia.

Email: thomas.anthopoulos@kaust.edu.sa

Keywords: Photonic curing, metal oxide semiconductors, metal oxide dielectrics, thin-film transistors, metal oxide heterojunctions

ABSTRACT

Solution-processed metal oxide thin-film transistors (TFTs) represent a promising technology for applications in existing but also emerging large-area electronics. However, high process temperatures and lengthy annealing times represent two remaining challenges. Different approaches aiming to address these challenges have been proposed but progress remains modest. Here, we describe the development of high electron mobility metal oxide TFTs based on photonically converted $\text{Al}_2\text{O}_3/\text{ZrO}_2$ and $\text{In}_2\text{O}_3/\text{ZnO}$ bilayers acting as the high- k dielectric and electron-transporting channel, respectively. Sequential solution-phase deposition and photonic processing lead to low substrate temperature ($<200^\circ\text{C}$) while minimizing the overall process time to less than 60 s without compromising the quality of the formed layers. The bilayer $\text{Al}_2\text{O}_3/\text{ZrO}_2$ dielectric exhibits low leakage current density ($10^{-6} \text{ A cm}^{-2}$ at 1 MV cm^{-1}), high geometric capacitance ($\approx 120 \text{ nF cm}^{-2}$) and breakdown electric field of $\approx 1 \text{ MV cm}^{-1}$. Combining $\text{Al}_2\text{O}_3/\text{ZrO}_2$ with a photonically converted $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction channels, results in TFTs with high electron mobility ($19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), low operation voltage ($\leq 2 \text{ V}$), high current on/off ratio ($>10^6$), and low subthreshold swing (108 mV dec^{-1}), that can be manufactured even onto thermally sensitive polymer substrates. The work is a significant step towards all-photonic processed metal oxide electronics.

1. Introduction

Ongoing technological and product developments provide the driving force towards thin-film transistors (TFTs) technologies with improved performance characteristics and manufacturability. Since their debut as channel materials in TFTs,^[1] metal oxide semiconductors have quickly become the subject of intense research due to their outstanding electrical and optical properties.^[2–4] There are various methods that can be used to grow metal oxide semiconductors the most common of which is via gas phase techniques such as physical vapor deposition (PVD),^[5] chemical vapor deposition (CVD),^[6] and atomic layer deposition (ALD).^[7] However, solution-based manufacturing techniques promise several advantages such as higher throughput and easier scalability for a range of envisioned inexpensive large-area electronic applications.^[8,9]

To reach comparable performance to vacuum-processed metal oxide TFTs, solution-processed oxides typically rely on high-temperature thermal annealing (>400 °C) over long time scales (hours). Not only does this step increase the process time and energy consumption, but it also restricts the choice of substrate materials. For these reasons, alternative methods have been explored.^[9,10] Among those, new chemical routes using, for example, nitrate-based precursors^[11], combustion synthesis^[12] or novel post-annealing techniques such as UV-processing, plasma or microwave treatments have been investigated^[13–15] for both dielectric and semiconductor metal oxide materials. Although significant improvements have been made to decrease the fabrication temperatures and process times, still only a few methods satisfy these requirements.

Photonic sintering is a post-processing method that has recently been attracting increasing attention as an alternative to conventional thermal annealing.^[16–18] In its simplest form, short pulses (μ s to ms) of high-intensity white light (broad spectrum of 200–1100 nm) generated by a xenon flash lamp are directed towards the substrate. Absorption of the light by the material(s) deposited on the substrate (metals or functional materials) can result in a

dramatic increase of the temperature to over 1000 °C for a short period of time that is comparable to the pulse duration. Most importantly, during the process, the substrate remains at low temperatures due to the short light exposure time and the mismatches of thermal equilibrium times of the absorber and the substrate materials.^[17] Although material combinations with different thermal expansion coefficients can lead to thermomechanical stress formation during the process, this can be mitigated by adequately tuning the process parameters (optical power density, number of shape of flashes and the frequency of optical pulses). Indeed, due to its fast and large area processing capability, the flash light annealing technique was already demonstrated for roll-to-roll (R2R) fabrication, specifically for the conversion of metal inks into highly conductive patterns.^[16,19] Apart from metal inks, a particular advantage of photonic curing over other low-temperature processing techniques is that it provides a significantly faster conversion from the precursor solution into solid thin layers while very high temperatures are localized only on the surface of the absorber element for the solution-based thin film fabrication. The rapid nature of the photonic process and its compatibility with a broad range of inexpensive substrate materials, such as a range of polymers, makes it an appealing fabrication method for high throughput manufacturing.

Here we report the rapid manufacturing of solution-processed, low operating voltage metal oxide TFTs where the dielectric and the semiconducting channels are both processed via photonic processing in ambient atmosphere. Within the group of metal oxide-based dielectrics, ZrO_2 and Al_2O_3 are well studied materials. While ZrO_2 has a higher permittivity (25) than Al_2O_3 (9), its lower band gap (5.8 vs. 9 for Al_2O_3) can result in higher leakage currents, especially for thin-films.^[20] To mitigate this problem and simultaneously achieve a high capacitance, the usage of homo- or heterojunction bilayer dielectric layers was suggested.^[21,22] We adopted a similar approach and explored the use of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ bilayer dielectric layers. The bilayer gate dielectric of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ was first grown on aluminum (Al) gate electrodes via sequential spin coating and flash annealing (for a duration of 16 s). Using the same steps, a low-dimensional

channel comprising an $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction,^[23] was then grown atop the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ dielectric. This specific combination of materials and stacking sequence for the active channel, i.e. $\text{In}_2\text{O}_3/\text{ZnO}$, was chosen based on multiple previous studies showing the enhanced properties compared to single layer channels.^[23–26]

Structural and electrical analysis of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ dielectric reveals the presence of a bilayer structure that exhibits low leakage current ($10^{-6} \text{ A cm}^{-2}$), high breakdown field ($\approx 1 \text{ MV cm}^{-1}$), smooth surface roughness (0.43 nm) and high geometrical capacitance ($\approx 120 \text{ nF cm}^{-2}$). As-prepared $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction TFTs exhibit n-channel characteristics with low voltage operation ($\pm 2 \text{ V}$) and high electron mobility ($19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$); an effect attributed to the formation of quasi-two-dimensional electron gas (q2DEG) confined at the $\text{In}_2\text{O}_3/\text{ZnO}$ interface. The presence of a q2DEG was corroborated experimentally via carrier profiling capacitance-voltage (C-V) measurements.

2. Results and discussion

2.1. Photonic curing of metal oxide layers

Figure 1 depicts the fabrication steps used to fabricate the metal oxide TFTs. A bottom-gate, top-contact transistor configuration was employed and combined with bilayer $\text{Al}_2\text{O}_3/\text{ZrO}_2$ dielectric^[21] and high mobility heterojunction $\text{In}_2\text{O}_3/\text{ZnO}$ ^[4] channels. During photonic treatment the Al layer plays a dual role, first acting as the gate electrode and secondly as the light absorber which heats-up and converts the precursor layer deposited on top of it.^[23] In brief, device fabrication (**Figure 1**) starts with the spin casting of the desired precursor solution followed by a drying step (step 1). Next, the sample is placed in close proximity to the xenon lamp (step 2) and subjected to pulse(s) of light of varying intensity and duration (see *Experimental*). During illumination, the gate electrode absorbs part of the light which raises the temperature of its surface rapidly whilst the substrate remains significantly cooler. The sample is then left to cool for a few seconds at room temperature (step 3). Under optimal processing

conditions, the precursor layer deposited atop the Al electrode converts fully to the thermally stable metal oxide phase. Steps 1 to 3 can be repeated numerous times allowing for accurate control of the stoichiometry and layer thickness of the multilayer oxides.

During photonic processing of the Al_2O_3 layer, we observed a strong correlation between the Al thickness and the optimal molarity of the aluminum oxide precursor formulation used. Non-optimized conditions led to Al electrode delamination (ablation) and the formation of partially destroyed gate-dielectric structures. **Table S1** and **Figure S1** (*Supporting Information*) summarize the effect of electrode thickness and molarity of the precursor formulation processed at a constant illumination intensity. The results reveal that use of a higher molarity $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursor formulation in combination with thinner Al gate electrodes leads to pronounced gate ablation (**Figure S1**). **Table 1** summarizes the materials and the corresponding processing conditions used to successfully convert the different precursors to the targeted metal oxides.

Table 1. Summary of the energy, pulse duration and the number of pulses used for the different metal oxides. For all oxide layers, the fire rate was kept at 1.2 Hz and the applied voltage 600 V.

Material	Energy density (J cm^{-2})	Pulse length (μs)	Number of pulses
Al_2O_3	1.84	250	20
ZrO_2	1.84	250	20
In_2O_3	4.44	600	30
ZnO	4.44	600	10

The *SimPulse* software tool was used to simulate the temperature evolution on the aluminum electrode surface (**Figure 2**).^[27] Due to the mismatch of thermal conductivities between Al and the glass substrate, the supplied optical energies are sufficient to increase the

temperature of Al while maintaining the substrate temperature low. For the growth of the dielectric layers on Al, the simulations suggest that temperatures $>500\text{ }^{\circ}\text{C}$ can easily be reached within 16 s (20 pulses) with the substrate temperature remaining $<120\text{ }^{\circ}\text{C}$ (**Figure 2a and 2b**). Considering the time scale of the process and the low substrate temperature, the fabrication conditions appear to be compatible with temperature-sensitive substrate materials such as plastics.^[3] Interestingly, **Figure 2c** shows that the ZrO_2 surface can momentarily reach temperatures in excess of $1000\text{ }^{\circ}\text{C}$ within 25 s. In the latter case, however, the substrate temperature increases as well reaching $300\text{ }^{\circ}\text{C}$. These results highlight the effectiveness of the xenon flash lamp to rapidly deliver energy to thin Al electrodes that act as micro-hotplates. Even though the same xenon lamp-driving voltage and pulse length were used to process the ZnO layer, a lower number of pulses was required to reach sufficiently high conversion temperatures, owing to its different optical properties and precursor chemistry^[21] (**Figure 2d**).

Thermogravimetric analysis (TGA) was used to study the decomposition temperatures of the various precursors. With the exception of ZnO, all precursors show dehydroxylation and condensation at $\geq 250\text{ }^{\circ}\text{C}$ (**Figure S2**). No such transition is observed for ZnO due to the specific chemistry employed. These results together with the *SimPulse* simulations, suggest that the temperatures required for dehydroxylation and condensation of the metal oxide precursors can easily be reached during photonic processing.

X-ray photoelectron spectroscopy (XPS) was used to monitor the degree of chemical conversion of the individual oxides before and after photonic treatment by studying the evolution of the O 1s spectra (see **Figure S3 a-d** and **Table S2**). The dominant peak between 531.5 and 530.5 eV is attributed to metal-oxygen-metal bonds,^[28,29] while the 2nd and 3rd peaks can be assigned to hydroxide and nitrate groups inside the thin film, respectively.^[30] As spun films dried at $130\text{ }^{\circ}\text{C}$ show higher amounts of hydroxide groups in Al_2O_3 , and both hydroxide and nitrate for In_2O_3 layers, respectively. Upon flashing all oxide precursor layers show reduced intensities in the corresponding M-OH and O- NO_3 peaks accompanied by increased M-O signal

intensities. Even though relatively high amounts of hydroxide groups may be observed right after the flashing of individual layers, these values will be lowered due to further processing of subsequent layers atop.

2.2. Photonic processing of multilayer metal oxide dielectrics

The use of high band-gap materials as gate dielectrics in transistors is beneficial due to low leakage currents. Al_2O_3 is a widely used gate dielectric in metal oxide TFTs as it combines a high band gap ($\approx 9 \text{ eV}$)^[20] with abundance and processing versatility. Unfortunately, its relatively low dielectric constant ($k = 9$) leads to lower geometrical capacitance as compared to other high- k metal oxides such as ZrO_2 and HfO_2 . ZrO_2 , in particular, has been attracting increasing attention in recent years due to its processing simplicity and very high relative permittivity ($\kappa = 25$).^[31,32] However, its relatively small band gap ($\approx 5.8 \text{ eV}$) often results in higher leakage currents and adverse effects on device performance. A simple approach to overcome this issue is by using multilayer dielectrics.^[22,33,34] **Figure 3a** shows a set of current-voltage (J - V) characteristics for metal/insulator/metal (MIM) devices based on photonicallly converted $\text{Al}_2\text{O}_3/\text{ZrO}_2$ bilayer as the dielectric. All devices show similar J - V characteristics with low leakage currents ($< 10^{-5} \text{ A cm}^{-2}$) and breakdown fields in the range $0.8\text{--}1 \text{ MV cm}^{-1}$. The fluctuations seen in the latter are attributed to non-uniformities associated with the Al_2O_3 layer and will be discussed later.^[35] In comparison with $\text{Al}_2\text{O}_3/\text{ZrO}_2$ bilayer dielectric, the single layers of Al_2O_3 and ZrO_2 showed high leakage current densities (see **Figure S4**). Because of this it was deemed unsuitable for application on its own.

Capacitance-voltage (C - V) and capacitance-frequency (C - f) measurements performed on the same MIM structure reveal a high capacitance value of $\approx 118 \text{ nF cm}^{-2}$ (**Figure 3b**) which remains stable with respect to the applied voltage and increasing frequency up to 7 MHz (**Figure 3c**). We attribute the good dielectric properties to the successful precursor decomposition and layer densification during photonic treatment. To verify this hypothesis we

examined the surface topography of all photonicallly processed layers via intermittent atomic force microscopy (AFM). **Figure 4** shows AFM images of the surface topographies for the various layers measured after deposition. Bare aluminum (**Figure 4a**) exhibits a relatively rough surface with a root mean square roughness (σ_{RMS}) of 1.81 nm, which is common for thermally evaporated Al.^[22] The surface of the photonicallly converted Al_2O_3 layer appears amorphous and retains a relatively high surface roughness of $\sigma_{\text{RMS}} = 1.6$ nm (**Figure 4b**). Subsequently deposited ZrO_2 , on the other hand (**Figure 4c**), exhibits significantly smoother surface with a drastically reduced σ_{RMS} of 0.43 nm. The positive effect of channel interface planarization was investigated in our previous study^[22] and is critical for the formation of a well-defined transistor channel. **Figures 4d** and **4e** show the topography AFM images for the photonicallly processed In_2O_3 and ZnO layers, respectively, atop the bilayer dielectric. In_2O_3 exhibits a smooth surface with $\sigma_{\text{RMS}} = 1.07$ nm as compared to ZnO ($\sigma_{\text{RMS}} = 1.85$ nm). These findings are in agreement with previous reports on ZnO, which always revealed the presence of a strongly textured surface.^[23,26] The differences in the AFM topographies between the various photonicallly processed layers are clearer in the height histogram of **Figure 4f**.

The electron transport in single-layer In_2O_3 and ZnO transistors as well as in $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction transistors, was studied in a bottom-gate, top-contact (BG-TC) device architecture. **Figure 5a-c** show sets of the corresponding transfer characteristics. All TFTs exhibit n-channel behavior and operate at low voltages in the range -0.5 to 2 V. Gate leakage currents at maximum V_G were on the order of 100 nA or below in all cases. While ZnO and $\text{In}_2\text{O}_3/\text{ZnO}$ devices show negligible hysteresis, this is not the case for In_2O_3 TFTs. We attribute this to charge trapping at states located in the In_2O_3 surface, which can be filled or passivated when ZnO is deposited atop in a subsequent step. The threshold voltage (V_T) of each devices is also different with the lowest value of 0.5 V measured for the $\text{In}_2\text{O}_3/\text{ZnO}$ TFT (**Figure 5d**), which also indicates a higher electron density in the channel.^[26,36,37]

Following the growth of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ bilayer dielectric, deposition of the single layer of In_2O_3 was optimized by tuning the energy density of the flash light while keeping the pulse length and number of flashes constant (**Figure S5a**). The resulting In_2O_3 TFTs exhibit an electron saturation mobility value of $5.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is significantly higher than ZnO transistors ($1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The relatively low mobilities are attributed to structural and/or chemical defects present in the channel^[38] and are comparable with values reported previously for solution-processed TFTs prepared via thermal annealing.^[34]

Optimization of the operating characteristics of the $\text{In}_2\text{O}_3/\text{ZnO}$ devices, on the other hand, was achieved by tuning the number of pulses while keeping the energy density of flashes and pulse length constant during the processing ZnO (**Figure S5b**). Resulting $\text{In}_2\text{O}_3/\text{ZnO}$ TFTs exhibit a significantly higher mobility of up to $19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; that is $>3\times$ higher than single-layer In_2O_3 and $19\times$ higher than ZnO devices. The higher electron mobility and lower V_T are consistent with the existence of a q-2DEG confined at the $\text{In}_2\text{O}_3/\text{ZnO}$ heterointerface in agreement with previous reports.^[26,36,39] Moreover, $\text{In}_2\text{O}_3/\text{ZnO}$ TFTs exhibit a high channel current on/off ratio of 1.4×10^6 and a subthreshold swing of 108 mV/dec. Furthermore, the output characteristics of the TFTs exhibit good saturation with no signs of injection barriers (**Figure 5e**).

To better understand the origin of the higher electron mobility in $\text{In}_2\text{O}_3/\text{ZnO}$ TFTs, we measured the electron concentration as a function of depth across the heterojunction channel using C-V measurements. **Figure 6a** shows the C-V characteristics measured for a metal-insulator-semiconductor (MIS) capacitor where both electron accumulation and depletion regimes can be identified.^[36] From the C-V characteristics, it is possible to study the distribution apparent electron concentration (N_{C-V}) across the channel using previously published methods.^[36] **Figure 6b** shows the N_{C-V} versus channel layer depth with zero distance representing the position of the top semiconductor-Al electrode interface.^[40] Evidently, N_{C-V} shows a distinct peak at $\approx 4 \text{ nm}$ from the channel interface, which correlates well with the

expected location of the $\text{In}_2\text{O}_3/\text{ZnO}$ heterointerface. Although the shape of the peak in $N_{\text{C-V}}$ would be expected to be very sharp for an atomically-flat interface, its broader nature indicates the existence of interface roughness. This observation agrees with the surface height histograms shown in **Figure 4f**, which show that the topography of ZnO and In_2O_3 fluctuate between 4 and 6 nm. Considering the low-dimensionality of the heterojunction channel, these results can be considered to be in good agreement. Overall, electrical characterization of the $\text{In}_2\text{O}_3/\text{ZnO}$ TFTs provides direct evidence of a highly anisotropic distribution of electrons in the out-of-plane direction of the heterojunction channel corroborating the existence of a q-2DEG at the critical heterointerface (see **Figure S6**).^[26]

To gain further insights into the nature of the $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction formed via sequential solution-processing and photonic sintering, we performed cross-sectional high-resolution transmission electron microscopy (HRTEM). **Figure 7a** shows the cross-sectional HRTEM image of the channel region, where the various layers can be discerned. Regions of the Al gate electrode appear to have melted and recrystallized during photonic processing as clearly visible in **Figure 7a**. The total thickness of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ bilayer is around 30 nm, while that of the $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction channel varies between 13-18 nm (**Figure 7b**). Combining scanning TEM (STEM) and electron energy loss spectroscopy (EELS) analysis (**Figure 7c**) allows the demarcation of the various metal oxide layer (i.e. Al_2O_3 , ZrO_2 , In_2O_3 , ZnO). Al_2O_3 and ZrO_2 appear to be ≈ 25 and ≈ 4 nm-thick, respectively, with some evidence of intermixing. On the other hand, the In_2O_3 and ZnO layers are ≈ 5 and ≈ 8 nm, respectively (**Figure 7b**). Possible reasons why the individual layers/interfaces are not clearly distinguishable, as compared to previous reports,^[26] is the high surface roughness of the underlying material (e.g., evaporated Al gate electrodes vs. SiO_2), and/or the rapid nature of the chemical conversion occurring upon photonic processing. Despite that, however, the EELS data in **Figure 7c** provide direct evidence of the existence of discrete oxide layers with the expected

elemental compositional order i.e., Al, Zr, In and Zn, with oxygen (O) being present throughout the multilayer structure.

To demonstrate the compatibility of photonic processing with temperature-sensitive substrates, we fabricated $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction TFTs on the bilayer high- k dielectric, on polyethylene naphthalate (PEN) substrates without using any thermal buffer layer. Due to the different thermal properties of PEN to those of glass, the possible thermal stress is more pronounced given the same flashing parameters. This problem could be overcome by inserting a buffer layer, such as SiO_2 or polyimide (PI),^[30] between substrate and metal or the tuning of flashing parameters for the temperature sensitive substrates. However, the insertion of such buffer layer increases fabrication complexity as it requires an extra fabrication step and for this reason it was not pursued here. Instead, a lower optical energy density of 1.1 J cm^{-2} and 60 pulses (2 ms pulse length) at a fire rate of 0.1 Hz, were employed (**Figure S7**). **Figure 8a-b** shows the transfer characteristics and a photograph of the $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction transistor arrays based on $\text{Al}_2\text{O}_3/\text{ZrO}_2$ dielectric fabricated on flexible PEN substrate, respectively. The transistors exhibit a maximum electron mobility of $2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, threshold voltage of 0.86 V, subthreshold swing (SS) of 123 mV and channel $I_{\text{ON}}/I_{\text{OFF}}$ ratio of $\approx 10^5$. The difference in performance between TFTs fabricated on glass and PEN substrates is most likely attributed to the different temperature gradients formed on the surface of the aluminum gate electrode and the increased surface roughness introduced by the PEN substrate as compared to the much smoother glass surface. One important difference is that in the case of glass, significantly higher optical energy intensities can be used without damaging the substrate due to its higher thermal conductivity. This, however, is not the case for PEN due to its lower thermal conductivity. As such, the maximum attainable device performance is limited by the mismatch in the thermal properties between the absorber (i.e. Al electrode in this case) and the substrate materials.

4. Conclusions

We have demonstrated the ability to rapidly manufacture high electron mobility $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction transistors using the high- k bilayer dielectric $\text{Al}_2\text{O}_3/\text{ZrO}_2$ via photonic processing over glass and flexible substrates. We achieved this using a patterned Al electrode acting simultaneously as the gate and optical energy absorber that thermally converts the spin-cast metal oxide precursor deposited atop to the targeted metal oxide. Unlike conventional thermal annealing, photonic processing occurs at ultra-short time scales –milliseconds to seconds as compared to tens of minutes– without adverse effects on the transistor characteristics. Importantly, the photothermally induced precursor conversion can be repeated many times allowing for sequential deposition of different materials on a variety of substrates, including temperature-sensitive polymers. Heterojunction $\text{In}_2\text{O}_3/\text{ZnO}$ TFTs utilizing the high- k bilayer dielectric $\text{Al}_2\text{O}_3/\text{ZrO}_2$ were shown to exhibit electron mobility values up to $19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when compared to TFTs made with single-layer In_2O_3 ($5.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and ZnO ($1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Finally, the same $\text{Al}/\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{In}_2\text{O}_3/\text{ZnO}$ -based TFTs were fabricated on PEN substrates, further showcasing the potential of photonic processing as a method for large-area manufacturing of future oxide electronics over arbitrary substrate materials.

Experimental Section

Precursor preparation: For the deposition of Al_2O_3 , ZrO_2 and In_2O_3 , 2-methoxyethanol solutions containing aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98 % Sigma–Aldrich), zirconium acetylacetonate ($\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$, 99 % Sigma–Aldrich) and indium nitrate ($\text{In}(\text{NO}_3)_3$, 99.99%; Indium Corporation) at concentrations of 100, 25 and 20 mg mL^{-1} , respectively, were employed. The solutions were subjected to 60 °C heating with vigorous stirring overnight before use. The ZnO precursor was prepared by dissolving ZnO hydrate ($\text{ZnO} \cdot x\text{H}_2\text{O}$, 97%; Sigma–Aldrich) in ammonium hydroxide (50% v/v; Alfa Aesar) at a concentration of 7 mg mL^{-1} at room temperature and stirring overnight.

Transistor Fabrication: Borofloat glass of 1.1 mm thickness was used as the substrate material for device fabrication. Glass substrates were cleaned by ultrasonication in DI water, acetone and isopropanol for 10 min each and dried in a nitrogen stream. As the final step of cleaning, a UV/ozone treatment was applied for 5 minutes to remove any residual organic from the surface. Thermally evaporated 100 nm-thick Al was used as combined gate electrodes and as the light absorber element for the photonic curing of dielectric and semiconductor layers that were sequentially deposited atop. The electrode was deposited by thermal evaporation at the rate of 2 nm s^{-1} under a high vacuum of $<10^{-6}$ torr. Prior to spin casting of the metal oxide solutions, Al electrodes were UV/ozone treated to enhance the wettability. All metal oxide precursors were spin-coated at 4000 rpm for 30 s. For the fabrication of dielectric, spin casting of precursor solutions for Al_2O_3 and ZrO_2 was repeated 5 times for each material in order to increase the overall layer thickness. After deposition, the films were baked at 130°C for 6 min to drive out the solvent. Next, the photonic curing step(s) was applied to the dried samples using a Novacentrix Pulse Forge 1300 system. The temperature distribution over the Al surface was simulated using their SimPulse^[27] software. The flashing conditions for Al_2O_3 and ZrO_2 dielectric layers were as follows: optical energy of 1.84 J cm^{-2} , pulse length of $250 \mu\text{s}$ and the number of pulses was kept to 20. Following the deposition of the gate dielectric, an In_2O_3 layer was spin-cast inside a nitrogen atmosphere. The as-cast precursor layer was first dried at 130°C for 6 min and then flashed with 30 pulses using optical energy of 4.44 J cm^{-2} with a pulse length of $600 \mu\text{s}$. For the ZnO layer, spin-coating was conducted in ambient environment and the film was dried at 110°C for 6 min. Dry ZnO layers were then subjected to 10 pulses of the same energy and duration as for the In_2O_3 layer. Finally, 40 nm-thick Al source and drain (S-D) electrodes were deposited via thermal evaporation through a shadow mask. The transistors were electrically characterized in a nitrogen atmosphere using a Keysight B2912A source-meter. The field-effect electron mobility was extracted from the transfer characteristic of the transistors using:

$$\mu_{sat} = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{D(sat)}}}{\partial V_G} \right)^2 \quad (1)$$

where L and W are the channel length and width, respectively, C_i is the geometric capacitance of the gate dielectric, $I_{D(sat)}$ is the current in the saturation regime, and V_G is the gate voltage applied between the gate (G) and the source (S) electrode.

Transistor Fabrication on PEN Substrate: For the fabrication of multilayer transistor over PEN substrate, the same precursor solutions and spin coating parameters were used for all layers as for the glass substrate. Considering the thermal properties of PEN, drying temperature after spin coating was kept 60 °C for 30 minutes. Differently, the optical energy of 1.1 J cm⁻², 2000 μs pulse length, 300 V and 60 pulses with the fire rate at 0.1 Hz were used for all the processed layers.

Dielectric characterization: The metal oxide dielectrics were characterized via capacitance-voltage (C-V) measurements using metal-insulator-metal (MIM) and metal-dielectric-semiconductor (MIS) structures with a Keysight B1500A semiconductor parameter analyzer. The capacitance-frequency (C-f) measurements were carried out at frequencies in the range 10³-10⁷ Hz. The leakage current density was evaluated using a MIM structure that was fabricated along the TFTs.

Surface analysis of the deposited layers: Surface roughness and topography of the individual layers were studied by atomic force microscopy (AFM) in tapping mode using a Bruker Dimension Icon with ScanAsyst®. In parallel to AFM analysis, the scanning electron microscopy (SEM) surface images of individual layers were taken with a Carl Zeiss URIGA® CrossBeam® Workstation using in-lens detectors with 5 kV acceleration voltage and 6 mm working distance.

Transmission electron microscopy: High-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) were also employed. Sample preparation was carried out using a Ga focused ion beam (FIB) in a scanning electron

microscope (SEM) (Helios 400s, FEI) equipped with a nanomanipulator (OmniProbe, AutoProbe300). A thin 2 nm layer of iridium was sputtered followed by the deposition of carbon and platinum protective layers in the SEM. The sample was then milled with the FIB down to the required thickness. The lamella was then extracted and attached to a copper TEM grid using established protocols. The lamella was thinned down at 30 kV and various currents (2.8-93 pA). At the final stage of the sample preparation, the lamella was cleaned with the ion beam at low voltages (2-5 kV) to remove any contamination. A transmission electron microscopy (Titan 80-300, FEI) with 300 kV was used for cross-sectional HRTEM imaging. The EELS elemental map was obtained with Gatan Imaging Filter (GIF) Quantum 966, scanning TEM (STEM).

X-ray photoemission spectroscopy: XPS measurements were carried out in an MXPS (Omicron) chamber at base pressure of 10^{-9} mbar equipped with a X1000 X-ray source (Omicron) and sphera II multi-channeltron analyser (Omicron), in addition a cold cathode ion source (ISE-5, Omicron) was used for preparation of a clean silver surface for calibration. The source was a monochromated Al K α 1486.7 eV at a power of 389.7 W (15 kV, 26 mA) with a source to sample angle of 13°. The photoelectrons were collected from the samples to analyzer angle of 87° and a tolerance of 7°, at constant pass energy of 15 eV (narrow scans) and 50 eV (survey scans). XPS spectra were analysed in Casa XPS. The spectra binding energy was first calibrated with respect to clean silver 3d core line and were calibrated with respect to the adventitious carbon C1s peak $\approx$ 284.7 eV to account for surface charging. Fitting of spectra was performed using a Shirley baseline and Gaussian-Lorentzian (GL) spectral function and are presented normalized by area.

Thermogravimetric analysis (TGA): TGA of all precursors was performed using a TGA analyzer (STA 449 F3 Jupiter from NETZSCH) in the air with a heating rate of 20 °C min⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors are grateful to KAUST for the financial support.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] K. Nomura, *Science*. **2003**, *300*, 1269.
- [2] E. Fortunato, P. Barquinha, R. Martins, *Adv. Mater.* **2012**, *24*, 2945.
- [3] L. Petti, N. Münzenrieder, C. Vogt, H. Faber, L. Büthe, G. Cantarella, F. Bottacchi, T. D. Anthopoulos, G. Tröster, *Appl. Phys. Rev.* **2016**, *3*, 021303.
- [4] D. Khim, Y.-H. Lin, S. Nam, H. Faber, K. Tetzner, R. Li, Q. Zhang, J. Li, X. Zhang, T. D. Anthopoulos, *Adv. Mater.* **2017**, *29*, 1605837.
- [5] E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Gonçalves, A. J. S. Marques, L. M. N. Pereira, R. F. P. Martins, *Adv. Mater.* **2005**, *17*, 590.
- [6] Z. Fan, D. Wang, P.-C. Chang, W.-Y. Tseng, J. G. Lu, *Appl. Phys. Lett.* **2004**, *85*, 5923.
- [7] J. Sheng, T. Hong, H.-M. Lee, K. Kim, M. Sasase, J. Kim, H. Hosono, J.-S. Park, *ACS Appl. Mater. Interfaces* **2019**, *11*, 40300.
- [8] S. R. Thomas, P. Pattanasattayavong, T. D. Anthopoulos, *Chem. Soc. Rev.* **2013**, *42*, 6910.
- [9] J. W. Park, B. H. Kang, H. J. Kim, *Adv. Funct. Mater.* **2019**, *1904632*, 1904632.
- [10] K. K. Banger, Y. Yamashita, K. Mori, R. L. Peterson, T. Leedham, J. Rickard, H.

- Sirringhaus, *Nat. Mater.* **2011**, *10*, 45.
- [11] A. Liu, G. Liu, H. Zhu, B. Shin, E. Fortunato, R. Martins, F. Shan, *RSC Adv.* **2015**, *5*, 86606.
- [12] M. G. Kim, M. G. Kanatzidis, A. Facchetti, T. J. Marks, *Nat. Mater.* **2011**, *10*, 382.
- [13] Y.-H. Kim, J.-S. Heo, T.-H. Kim, S. Park, M.-H. Yoon, J. Kim, M. S. Oh, G.-R. Yi, Y.-Y. Noh, S. K. Park, *Nature* **2012**, *489*, 128.
- [14] Y. M. Park, J. Daniel, M. Heeney, A. Salleo, *Adv. Mater.* **2011**, *23*, 971.
- [15] T. Jun, K. Song, Y. Jeong, K. Woo, D. Kim, C. Bae, J. Moon, *J. Mater. Chem.* **2011**, *21*, 1102.
- [16] E. Yarali, C. Koutsaki, H. Faber, K. Tetzner, E. Yengel, P. Patsalas, N. Kalfagiannis, D. C. Koutsogeorgis, T. D. Anthopoulos, *Adv. Funct. Mater.* **2019**, 1906022.
- [17] K. A. Schroder, *TechConnect Briefs* **2011**, *2*, 220.
- [18] K. Tetzner, K. A. Schroder, K. Bock, *Ceram. Int.* **2014**, *40*, 15753.
- [19] J. Perelaer, R. Abbel, S. Wünscher, R. Jani, T. van Lammeren, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 2620.
- [20] W. Xu, H. Wang, L. Ye, J. Xu, *J. Mater. Chem. C* **2014**, *2*, 5389.
- [21] Y. H. Lin, H. Faber, K. Zhao, Q. Wang, A. Amassian, M. McLachlan, T. D. Anthopoulos, *Adv. Mater.* **2013**, *25*, 4340.
- [22] A. D. Mottram, P. Pattanasattayavong, I. Isakov, G. Wyatt-Moon, H. Faber, Y.-H. Lin, T. D. Anthopoulos, *AIP Adv.* **2018**, *8*, 065015.
- [23] K. Tetzner, Y.-H. Lin, A. Regoutz, A. Seitkhan, D. J. Payne, T. D. Anthopoulos, *J. Mater. Chem. C* **2017**, *5*, 11724.
- [24] Y.-H. Lin, W. Li, H. Faber, A. Seitkhan, N. A. Hastas, D. Khim, Q. Zhang, X. Zhang, N. Pliatsikas, L. Tsetseris, P. A. Patsalas, D. D. C. Bradley, W. Huang, T. D. Anthopoulos, *Nat. Electron.* **2019**, *2*, 587.
- [25] D. Khim, Y. Lin, T. D. Anthopoulos, *Adv. Funct. Mater.* **2019**, *29*, 1902591.

- [26] H. Faber, S. Das, Y.-H. Lin, N. Pliatsikas, K. Zhao, T. Kehagias, G. Dimitrakopoulos, A. Amassian, P. A. Patsalas, T. D. Anthopoulos, *Sci. Adv.* **2017**, 3, e1602640.
- [27] M. J. Guillot, K. A. Schroder, S. C. Mccool, in *ASME 2012 International Mechanical Engineering Congress & Exposition IMECE2012*, ASME, New York, USA 2012, pp. 19–27.
- [28] S. Park, K.-H. Kim, J. Jo, S. Sung, K.-T. Kim, W. Lee, J. Kim, H. J. Kim, G. Yi, Y. Kim, M. Yoon, S. K. Park, *Adv. Funct. Mater.* **2015**, 25, 2807.
- [29] H. Faber, Y.-H. Lin, S. R. Thomas, K. Zhao, N. Pliatsikas, M. A. McLachlan, A. Amassian, P. A. Patsalas, T. D. Anthopoulos, *ACS Appl. Mater. Interfaces* **2015**, 7, 782.
- [30] N. M. Twyman, K. Tetzner, T. D. Anthopoulos, D. J. Payne, A. Regoutz, *Appl. Surf. Sci.* **2019**, 479, 974.
- [31] G. Adamopoulos, S. Thomas, P. H. Wöbkenberg, D. D. C. Bradley, M. A. McLachlan, T. D. Anthopoulos, *Adv. Mater.* **2011**, 23, 1894.
- [32] S. Park, C.-H. Kim, W.-J. Lee, S. Sung, M.-H. Yoon, *Mater. Sci. Eng. R Reports* **2017**, 114, 1.
- [33] J.-W. Jo, K.-H. Kim, J. Kim, S. G. Ban, Y.-H. Kim, S. K. Park, *ACS Appl. Mater. Interfaces* **2018**, 10, 2679.
- [34] M. U. Chaudhry, K. Tetzner, Y. H. Lin, S. Nam, C. Pearson, C. Groves, M. C. Petty, T. D. Anthopoulos, D. D. C. Bradley, *ACS Appl. Mater. Interfaces* **2018**, 10, 18445.
- [35] A. Liu, H. Zhu, H. Sun, Y. Xu, Y.-Y. Noh, *Adv. Mater.* **2018**, 30, 1706364.
- [36] Y. H. Lin, H. Faber, J. G. Labram, E. Stratakis, L. Sygellou, E. Kymakis, N. A. Hastas, R. Li, K. Zhao, A. Amassian, N. D. Treat, M. McLachlan, T. D. Anthopoulos, *Adv. Sci.* **2015**, 2, 1.
- [37] M. Lee, J. W. Jo, Y. J. Kim, S. Choi, S. M. Kwon, S. P. Jeon, A. Facchetti, Y. H. Kim, S. K. Park, *Adv. Mater.* **2018**, 30, 1.

- [38] H. Frenzel, A. Lajn, H. Von Wenckstern, M. Lorenz, F. Schein, Z. Zhang, M. Grundmann, *Adv. Mater.* **2010**, 22, 5332.
- [39] J. G. Labram, Y. H. Lin, T. D. Anthopoulos, *Small* **2015**, 11, 5472.
- [40] S. P. Voinigescu, K. Iniewski, R. Lisak, C. A. T. Salama, J. P. Noël, D. C. Houghton, *Solid State Electron.* **1994**, 37, 1491.

Figures

Figure 1. Processing steps used to fabricate metal oxide TFTs via photonic curing. (1) The spin casting of precursor solution onto pre-patterned/deposited Al gate electrodes. (2) Exposure of the sample to high-intensity light pulses generated by a xenon lamp. (3) The precursor film atop the Al electrode chemically converts to a dense solid oxide layer. (4) Transistor fabrication is completed with the deposition of aluminum (Al) source-drain electrodes via vacuum sublimation.

Figure 1. Temperature evolution on the surfaces of Al electrode (a), Al_2O_3 layer (b), ZrO_2 layer (c) and In_2O_3 layer (d) calculated using the *SimPulse* software and glass as the substrate material. The results were used as a guide to identify the processing conditions that will lead to successful chemical conversion of the corresponding precursor to the targeted metal oxide, namely Al_2O_3 (a), ZrO_2 (b) In_2O_3 (c), and ZnO (d). In all cases a fire rate of 1.2 Hz and 600 V were used.

Figure 2. (a) Leakage current density versus applied electric field for a set of similar MIM devices. Inset shows the Al/ Al_2O_3 / ZrO_2 /Al device architecture employed. (b) Capacitance-voltage characteristics for a representative Al/ Al_2O_3 / ZrO_2 /Al device measured using an AC signal frequency of 1 kHz with a peak-to-peak voltage of 100 mV. (c) Capacitance versus frequency in the range 10^3 - 10^6 Hz.

Figure 4. AFM images of the surface topographies of (a) Al electrode, (b) Al₂O₃, (c) ZrO₂, (d) In₂O₃ (e) ZnO layers deposited sequentially via spin-coating atop the Al layer and photonically treated at each step. (f) Height histograms of all layers.

Figure 5. Transfer characteristic of (a) In_2O_3 , (b) ZnO and (c) $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction transistors fabricated via photonic curing. (d) Plot of $(I_{\text{DS}})^{1/2}$ versus V_G for all three devices from which the electron mobility and V_T were extracted. (e) Representative output characteristics for a heterojunction transistor shown in (c).

Figure 6. (a) Capacitance-Voltage measurement obtained from the metal-insulator-semiconductor structure as indicated in the inset and (b) Free electron (N_{C-V}) profile as a function of depth from MIS structure.

Figure 7. (a-b) Low to high magnification cross-sectional HRTEM. (c) STEM images of the complete metal oxide layer channel stack processed sequentially via spin-coating and photonic curing. The layers labelled Ir, C and Pt are applied during the TEM sample preparation for the sole purpose of imaging and don't have a functional role. (c) STEM cross-section and elemental distribution analysis throughout the layers measured with EELS.

Figure 8. (a) Transfer characteristic of an $\text{In}_2\text{O}_3/\text{ZnO}$ heterojunction TFT utilizing $\text{Al}_2\text{O}_3/\text{ZrO}_2$ bilayer as the high- k dielectric, photonically processed on PEN substrate. (b) Photograph of TFT arrays processed on a flexible PEN substrate.

ToC Text

High electron mobility metal oxide transistors based on photonicallly-processed $\text{Al}_2\text{O}_3/\text{ZrO}_2$ and $\text{In}_2\text{O}_3/\text{ZnO}$ bilayers, acting as the high- k dielectric and electron-transporting channel, respectively, are demonstrated. The photonic-based conversion process enables rapid manufacturing of metal oxide transistors while simultaneously minimizing the thermal budget making it compatible with temperature-sensitive substrate materials.

Keyword: Photonic curing, metal oxide semiconductors, metal oxide dielectrics, thin-film transistors, metal oxide heterojunctions

Emre Yarali, Hendrik Faber, Emre Yengel, Akmaral Seitkhan, Kalaivanan Loganathan, George T. Harrison, Begimai Adilbekova, Yuanbao Lin, Chun Ma, Yuliar Firdaus, Thomas D. Anthopoulos

Low-Voltage Heterojunction Metal Oxide Transistors via Rapid Photonic Processing

Copyright WILEY-VCH Verlag GmbH & Co. KGaA, 69469 Weinheim, Germany, 2016.

Supporting Information

Low-Voltage Heterojunction Metal Oxide Transistors via Rapid Photonic Processing

Emre Yarali, Hendrik Faber, Emre Yengel, Akmaral Seitkhan, Kalaivanan Loganathan, George T. Harrison, Begimai Adilbekova, Yuanbao Lin, Chun Ma, Yuliar Firdaus, Thomas D. Anthopoulos*

Table S1. The qualitative assessment of Al ablation in combination with the precursor concentration and aluminum thickness during the fabrication of the Al_2O_3 layer.

Thickness of Al electrode (nm)	Concentration of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ precursor solution (mg/ml)	Ablation rate
40	100	Medium
100	100	None
100	250	High

Figure S1. Optical microscopy images of the flashed metal electrodes with (a) 40 nm aluminum electrode with 100 mg ml^{-1} $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ concentration, (b) 100 nm aluminum electrode with 100 mg ml^{-1} $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ concentration and (c) 100 nm aluminum electrode with 250 mg ml^{-1} $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ concentration.

Figure S2. Thermogravimetric analysis of the metal precursors of Al(NO₃)₃·9H₂O, Zr(C₅H₇O₂)₄, ZnO and In(NO₃)₃·xH₂O, respectively.

Figure S3. O 1s core level XPS spectra of (a) Al_2O_3 , (b) ZrO_2 , (c) In_2O_3 and (d) ZnO before and after flashing.

Table S2. Summary of the XPS results for the oxide layers before and after flash treatment.

	Dried			Flashed		
Material	M-O %	M-OH %	NO ₃ %	M-O %	M-OH %	NO ₃ %
Al ₂ O ₃	3.04	81.93	15.03	24.85	72.25	2.8
ZrO ₂	36.43	63.57	-	40.62	59.38	-
In ₂ O ₃	6.27	56.16	37.56	45.29	45.76	8.94
ZnO	48.3	51.2	-	57.9	42.1	-

Figure S4. The leakage current densities of single layer of Al₂O₃, ZrO₂ and bilayer Al₂O₃/ ZrO₂ recorded in metal/insulator/metal configuration.

Figure S5. The transfer characteristics of (a) single layer In₂O₃ TFTs with different flash light densities and the same number of flashes of 30 pulses, (b) In₂O₃/ZnO heterojunction TFTs with the different number of flashes and same energy density of 4.44 J/cm².

Figure S6. Energy band diagram of the In₂O₃/ZnO heterojunction.

Figure S7. The simulation of the surface temperature of the aluminum electrode (250 nm) and of the PEN substrate temperature, generated with the SimPulse software, was used for the precursor conversion to form $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{In}_2\text{O}_3/\text{ZnO}$ layers with a fire rate of 0.1 Hz, 2000 μs and 300 V, 60 pulses.