Supplementary Information

Spray-Combustion Synthesis. Efficient Solution Route to High-Performance Oxide Transistors

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Experimental Section

Metal Oxide film and transistor fabrication. Doped Si/SiO₂ wafers (300 nm, \( C_i = 10.5 \text{nF cm}^{-2} \) WRS Materials; solvent cleaned, then cleaned with an O₂ plasma for 5min) were used as the gate electrode/dielectric layer. For the other MO dielectrics, amorphous Al₂O₃ \( (C_i = 160\text{nF cm}^{-2}) \) and ZrO₂ \( (C_i = 255\text{nF cm}^{-2}) \) dielectric films were grown on the appropriate substrates as reported previously (see SI). In₂O₃, IZO, and IGZO films were deposited by SCS, spin-SC, sol-gel, all in a well-ventilated fume hood, or magnetron-sputtering as indicated below. Finally, 40nm Al source/drain electrodes \( (W/L = 1000\mu m/50\mu m) \) were evaporated through a shadow mask.

Precursor solutions for SCS and spin-CS. All reagents were used as received from Sigma-Aldrich. These solutions were prepared with In(NO₃)₃·xH₂O, Zn(NO₃)₂·xH₂O, and Ga(NO₃)₃·xH₂O in 2-methoxyethanol to yield 0.05 or 0.5 M solutions. For 0.05 [or 0.5] M solutions, 55 [or 110] µL NH₄OH and 100 [or 200] µL acetylactone were added to 10 [or 2] mL of the metal solutions and stirred overnight at 25°C. Prior to spin- or spray-coating, the precursor solutions were combined in the desired molar ratios and stirred for 2h. All depositions were carried out at RH<30%.

SCS: Substrates were maintained at 200-350 °C on a hot plate while 0.05M precursor solutions were loaded into the spray gun and sprayed intermittently (60s cycles) on the substrates until the desired thickness (20, 50nm) was obtained. The drop feature size is between 30 to 150 µm, depending on the processing temperature. The nozzle-substrate distance was 10-30cm.

Spin-CS: For 20nm thick (4 layers) devices, 0.05M precursor solutions were spin-coated at 3500rpm for 30s, and then annealed for 30min at 200-350°C; this was repeated 4x to achieve the desired thickness. For one-step 50nm single layer devices, precursor solutions with concentrations of 0.5M were spin-coated at 2000rpm for 60s, and then annealed for 30min at the desired temperature.

Spray: The precursor solution and coating process was identical to that of SCS but without acetylacetone.

Sol-gel: These solutions were prepared with In(NO₃)₃·xH₂O, Zn(NO₃)₂·xH₂O, and Ga(NO₃)₃·xH₂O
in 2-methoxyethanol with a concentration of 0.5M, and then stirred overnight at 25°C. Prior to
spin-coating, the precursor solutions were combined in the desired molar ratios and stirred for
2h. For one-step 50nm single layer films, the precursor solutions were spin-coated at 2000 rpm
for 60s, and then annealed for 30min at the desired temperature.

**Sputtering:** 50nm IGZO films were sputtered (1:1:1 target from Nikko Denko) using
magnetron-sputtering equipment (AIA International) with a base pressure <10⁻⁵Torr and a
Ar/O₂ mixture (20 sccm:1 sccm). After sputtering, the films were annealed at 350°C for 60 min.

**Al₂O₃ and ZrOₓ dielectric fabrication.** Amorphous Al₂O₃ and ZrOₓ dielectric films were grown
using a procedure reported previously: Al(NO₃)₃·xH₂O, ZrCl₄ and Zr(OCH(CH₃)₂)₄(CH₃)₂CHOH
were used as the precursor for Al₂O₃ and ZrO₂, respectively.[¹,²]

**Oxide film morphology characterization.** AFM film morphologies were imaged with a Veeco
Dimension Icon scanning Probe Microscope using tapping mode. SEM images were recorded
using a Hitachi S4800-II. XRD measurements were performed with a Rigaku ATX-G Thin Film
Diffraction Workstation using Cu kα radiation coupled to a multilayer mirror. For STEM and TEM
measurements, samples were prepared using both spin-coating (3500 rpm for 30 s, then
annealing for 30 min, repeated four times) and spray-coating (see Spray coating section below )
with 0.05 M precursor solution on NaCl substrates with either post annealing or situ annealing.
The prepared sample was then lifted with an OmniProbe nanomanipulator and transferred to a
semi-spherical Cu TEM grid. STEM imaging was conducted with a JEOL-2300F microscope, and
TEM imaging was conducted with a JEOL-2100F microscope. XPS (Omicron ESCA Probe)
characterization of In 3d, Ga 3d, Zn 2p, and O 1s signals were monitored on metal oxide/SiO₂
after surface cleaning.

**Electrical measurements.** TFT device characterization was performed on a customized probe
station in air with a Keithly 6430 subfemtometer and a Keithly 2400 source meter, operated by a
locally written Labview program and GPIB communication. For bias stress and ultra-low current
measurements a Keithley 4200 multi-channel electrometer was used. Four-probe conductivity
measurements were carried out using an Agilent electrometer.

**X-ray reflectivity measurements.** XRR of the four IGZO film samples were performed on the 18
kW Rigaku ATXG workstation at the J.B. Cohen X-ray lab at Northwestern University. Cu kα X-
rays (wavelength is $\lambda = 0.1541\ \text{nm}$) were generated and collimated to produce a monochromated beam of dimensions $5.0\text{mm} \times 0.1\text{mm}$ and $2 \times 10^8 \ \text{photons/sec}$ flux at the sample surface. The XRR data were modeled and fit by applying an Abeles matrix method used in the Motofit package to obtain the thickness, electron density, and interfacial roughness information of each layer.

**Mass density calculation by XRR:** The X-ray reflectivity $R(Q)$ as a function of momentum transfer modulus $Q = 4\pi \sin(2\theta/2) / \lambda$ can be modeled by

$$\frac{R(Q)}{R_F(Q)} = \left| \int \left( \frac{d\rho}{dz} e^{iQz} dz \right)^2 \right|$$

where $R_F(Q)$ is the Fresnel reflectivity from an ideal substrate (Si) mirror surface, and $\rho(z)$ is the electron density profile along the surface normal normalized to the substrate density. XRR analysis determines the film electron density ($\rho_e$), film thickness, and interfacial/surface roughness. For a given composition, the mass density ($\rho_m$) can be calculated from

$$\rho_m = \frac{\rho_e M}{N_e} \frac{1}{N_A}$$

where $M$ is molar mass, $N_e$ the total film electron number, and $N_A$ is Avogadro’s constant.

**Positron annihilation spectroscopy.** PAS was used to monitor the porosity of some selected IGZO films. In order to obtain depth-resolved data, positrons were implanted in the sample at various depths using a variable-energy positron beam at the VEPAS laboratory (LNESS Centre - Politecnico di Milano). The depth resolution of a variable-energy positron beam depends on the positron implantation-profiles of the so-called Makhov distribution, that is narrow at low positron implantation energy and broader at high implantation energy. The explored region after implantation depends on the positron and positronium diffusion length. Positronium diffusion depends on the pore dimensions and the pick-off conversion. A hyperpure Ge $\gamma$-ray detector was used to measure the spectrum of the annihilation radiation. This spectrum contains a peak centered at $511\ \text{keV}$, which comes from two-$\gamma$ positron-electron annihilation, and a continuous distribution below $511\ \text{keV}$, coming from three-$\gamma$ annihilation of positronium atoms formed at the open pores into the amorphous films. The two-$\gamma$ peak, which is broadened by the Doppler effect due to the motion of the electrons encountered by positrons, bears the
signature of the chemistry and defectivity of the material. The $S$-parameter corresponds to annihilation of positrons with valence electrons and Ps annihilation (para-Ps and ortho-Ps pick-off that annihilate in two-$\gamma$ rays). This parameter was taken in the energy range $511\pm 0.85$ keV. In the present work, the $S$-parameter was normalized to the Si bulk value ($S_r = S/S_{Si}$, with $S_{Si} \approx 0.54$).

An additional PAS parameter, sensitive to the presence of free volume and to the extension of inner pore surface, is the positronium fraction. Ps fraction measurements were performed using the well-known “3$\gamma$ method”\cite{4}. From the annihilation spectrum it is possible to obtain the $R(E)$ parameter,

$$ R(E) = \frac{V}{P} $$

where $P$ and $V$ are the integrated counts (after background subtraction) in the peak ($511\pm 4.25$ keV) and valley area above the Compton edge, from 350 keV up to 500 keV, of the energy $\gamma$ spectrum. When there is no pick-off annihilation, i.e., when the positronium is emitted in vacuum, the Ps fraction $F(E)$ can be obtained from $R(E)$ using the relationship:

$$ F(E) = \left[ 1 + \frac{P_1(R_1 - R(E))}{P_0(R(E) - R_0)} \right]^{-1} $$

where $P_0$ and $R_0$ are the parameters when the Ps fraction is nil ($F=0$) and $P_1$ and $R_1$ are the parameters when 100% of the positrons becomes positronium ($F=1$). The calibration for 0% and ~100% of Ps in vacuum was performed using a Ge single crystal (100) at 1000 K.

The PAS results ($F_{3\gamma}$ and $S_r$ parameters), as mentioned in the text, confirm that the SCS 1:0.1:0.29 and sputtered 1:1:1 films are the most compact. For a quantitative estimation, a fitting procedure represented by the continuous curves through the experimental points of the $S_r$ evolutions in Figure S17 (VEPFIT\cite{5}) was implemented. This software is a best fit procedure based on the solution of the diffusion equation in each layer of a heterostructure, taking into account the positron implantation-profiles dependent on energy.\cite{6} The mean positron implantation depth $Z_m$ depends on the positron implantation energy $E$ according to the formula,

$$ Z_m = \frac{A}{\rho} E^n $$
with \( n \) and \( A \) semi-empirical parameters (\( n= 1.6 \) and \( A= 40 \text{ nm g cm}^{-3} \text{ keV}^{-1.6} \)), \( \rho \) the mass density in g cm\(^{-3} \) and \( E \) in keV (this equation was used in Figure 4c for representing the PAS data as a function of the positron implantation depth). The fitting procedure is based on a model that schematically divides the explored regions in three layers: IGZO, SiO\(_2\) and the silicon substrate, separated by three interfaces (vacuum/IGZO –surface–, IGZO/SiO\(_2\) and SiO\(_2\)/Si). The interfaces were taken to be very thin \( \sim 1 \text{ nm} \) and completely absorbing, i.e. inside of them the positron diffusion length is <1 nm.\(^7\) The positron diffusion lengths \( L^+ \) in the IGZO films are about 11 nm (see Table S1) in both films, while the positronium diffusion lengths were 2(1) nm.

The thicknesses of the IGZO films were measured accurately by XRR with an absolute error of about 1 nm (see Table S1 and dashed line in Figure S17). Based on these thickness values, the mass densities of the films were estimated, minimizing the reduced chi-square statistics of the model fits \( \chi^2_R \). Figure S17 shows the \( \chi^2_R \) plots where the obtained values that minimize the fits are: \( \rho_{\text{sputt}} = 5.8(2) \text{ g cm}^{-3} \) and \( \rho_{\text{SCS}} = 6.4(2) \text{ g cm}^{-3} \). The IGZO films 1:1:1: spin-CS, sol-gel and SCS were also fit and the values of the number densities are: <5.2 g cm\(^{-3}\), <5.4 g cm\(^{-3}\), and 5.6 (2) g cm\(^{-3}\), respectively. In the case of spin-CS and sol-gel films the \( S_r \) parameter is under the saturation regime (an important amount of positronium -- para-Ps and ortho-Ps pick-off -- annihilates to two-gamma rays in the amorphous films) and, in these cases, the obtained diffusion lengths in the films are highly influenced by Ps diffusion. For this reason the number densities in spin-CS and sol-gel films are considered upper limits. The porosities of the 1:1:1 films (sol-gel, combustion, SCS and sputtering) were estimated considering the density of a IGZO single crystal (\( \rho_{\text{IGZO}} \sim 6.2 \text{ g cm}^{-3} \)).\(^6\) \( \rho_{\text{sol-gel}} >15\%; \rho_{\text{comb}} >16\%; \rho_{\text{SCS}} = 10(2)\% \) and \( \rho_{\text{sputt}} = 6(2)\% \). By comparison between the PAS results between sputtered 1:1:1 and SCS 1:0.1:0.29, we conclude that the porosity of the latter indium-rich film is approximately the same as the sputtered film, i.e. \( \sim 6\% \).

In order to obtain an estimate of the mean cavity size and other useful parameters, two porous film families were considered:

- **The most porous films (sol-gel, spin-SC and SCS 1:1:1).** According to the XRR estimates the porosity \( p \) of the sol-gel and spin-SC films is about 40\% (\( p= (1-\rho_m/\rho_{\text{SC}}) = V_v/V_f = \nu_v \), where \( \rho_m \) and \( \rho_{\text{SC}} \) are the mass densities measured in the film and of the single
crystals, respectively, $V_V$ and $V_T$ are the free and total volume, respectively, and $V_V$ is the free volume per volume unit. This high porosity allows us to hypothesize a high degree of pore connectivity. In this condition, the $P$s diffusion length is a good indication of the average pore size $\Phi$, which is around 2.5(5) nm. On the other hand, an estimation of the cavity number density $\eta$ let to verify the interconnectivity hypothesis. Considering that the porosity (or $V_V$) is equal to the number density of cavities multiplied by the unitary average free volume $V_U$ ($V_V = \eta V_U = \eta \frac{4}{3} \pi (\Phi/2)^3$, where $V_U \sim 10$ nm$^3 = 10^{-20}$ cm$^3$) $\eta$ is equal to $4 \times 10^{19}$ cm$^{-3}$. These values are within the condition of pore interconnection, i.e., according to the proposed approximation, it is frequent the superposition or packing of spheres of vacuum zones.

Following the same ideas, 1:1:1 SCS has a porosity $\sim10\%$, a mean pore size 1.5(5) nm and a number density of cavities $\sim6 \times 10^{19}$ cm$^{-3}$ ($V_U \sim 1.8$ nm$^3 = 1.8 \times 10^{-21}$ cm$^3$). In this condition the porous connectivity is low.

- **The most compact films** (sputtered 1:1:1 and SCS 1:0.1:0.29). From the $F_{3\gamma}$ measurements it is possible to obtain an upper-limit of the pore dimension of $\sim 1$ nm (where $F_{3\gamma} \rightarrow 0$, see manuscript). Besides, the minimum pore size in an amorphous film is about 4 Å (to be not considered as a vacancy or as a small vacancy cluster). The porosity of this films was estimated to be about 6% from PAS and XRR measurements. Thus, the number density is $\sim2 \times 10^{20}$ cm$^{-3}$ ($V_U \sim 0.3$ nm$^3 = 3 \times 10^{-22}$ cm$^3$, considering an average diameter of the cavity $\sim 7$-8 Å). In this case the possibility of pore interconnection is very low.

**C–V measurements and trap density extraction.** C–V measurements are made on MIS structures and with frequency kept low enough to monitor the trapping and detrapping mechanism. The MIS structure does not require frequencies as low as the TFTs because charges do not have to travel laterally from channel to the source/drain contacts. Therefore all measurements were made at 1 kHz. From the C–V data we can extract the surface potential, $\varphi_s$, (i.e., the potential at the semiconductor dielectric interface where $x = 0$). This comes from the surface charge accumulated, $Q$:

$$Q = C_i (V_g - \varphi_s)$$
Differentiating this w.r.t $V_G$ and knowing that the measured capacitance, $C$, will be $dQ/dV_G$, then:

$$\frac{\partial \varphi_s}{\partial V_G} = 1 - \frac{1}{C_i} \frac{dQ}{dV_G} = 1 - \frac{C}{C_i}$$

Therefore we can find $\varphi_s$ by integrating our capacitance normalized to the capacitance of the dielectric:

$$\varphi_s - \varphi_0 = \int_{V_b}^{V_a} \left(1 - \frac{C}{C_i}\right) dV_G'$$

Note that this requires an estimate of the flat-band voltage $V_{fb}$ which is taken as the point at which the $C$–$V$ data starts to rise. This could be a significant source of error as the surface potential is very sensitive to $V_{fb}$ and $C_i$. We can also find the surface potential gradient by applying Gauss’s Law at the semiconductor-dielectric interface:

$$\varepsilon_s \frac{\partial \varphi}{\partial x} |_{x=0} = \varepsilon_i \frac{V_G - \varphi_s}{t_i}$$

$\varepsilon_s$ = semiconductor dielectric constant

$\varepsilon_i$ = insulator dielectric constant

$t_i$ = insulator thickness

These data provide the boundary conditions for solving Poisson’s equation in the semiconductor. Poisson’s equation, where $n$ is the charge density, is:

$$\frac{\partial^2 \varphi(x)}{\partial x^2} = -\frac{n(x)}{\varepsilon_s \varepsilon_0}$$

The charge density, $n$, consists of the free and trapped carriers:

$$n_{\text{free}} = n_s \exp \left(\frac{q \varphi(x)}{kT}\right)$$

$$n_{\text{trap}} = \int D_{\nu}(\varphi(x)) dE$$

$D_{\nu}$ is the density of trap states. Therefore we are solving,

$$\varepsilon_s \varepsilon_0 \frac{\partial^2 \varphi(x)}{\partial x^2} + q n_s \exp \left(\frac{q \varphi(x)}{kT}\right) + q \int D_{\nu}(\varphi(x)) dE = 0$$

to get the potential distribution, $\varphi(x)$, in the semiconductor for each gate voltage.

However, $D_{\nu}$ is unknown and is sought. It is also a function of the potential, therefore we must iterate over each gate voltage solving the Poisson equation and estimate values of $D_{\nu}$ to obtain
the correct surface potential and potential gradient from the C–V data. The boundary conditions for the Poisson equation are:

\[ \varphi(0) = \varphi_s \]

\[ \frac{\partial \varphi}{\partial x_1^{i-x_i}} = 0 \]

The problem is that this is a non-linear second order partial differential equation and the solution can be unstable. It therefore requires small \( V_G \) steps and many iterations.
Figure S 1. **a**, Schematic reaction coordinate comparing the energetics of combustion synthesis and conventional sol-gel solution processing, and combustion reaction for a generic metal with nitrate acting as the oxidizer and acetylacetone as the fuel. **b**, Example of the conventional spin-coating/combustion process for metal oxide films deposition.
Figure S2. a-c. X-ray diffraction (XRD) patterns of various 20 nm thick oxide films for different combustion processing temperatures deposited using spin-coating and SCS. a, For In$_2$O$_3$ films. b, For IZO films. c, For IGZO films.
Figure S3. X-ray photoelectron spectra of 20 nm thick oxide films deposited at different processing temperatures. a, for In$_2$O$_3$. b, for IZO. c, for IGZO. 529.9± 0.1 eV: M-O-M lattice oxygen; 531.3 ±0.1 eV: M-OH metal hydroxide oxygen; 532.2 ± 0.1 eV: adsorbed oxygen species.
Figure S4. X-ray photoelectron spectroscopy (XPS) survey scans of the In 3d, Ga 3d, and Zn 2p peaks for combustion 20 nm thick IGZO films annealed at 300 °C: a, deposited by spin-coating, b, deposited by SCS.
Figure S5. Atomic force microscopy (AFM) images of 20 nm thick spin-coated a, In$_2$O$_3$, b, IZO, and c, IGZO films on SiO$_2$ annealed at the indicated temperatures.
Figure S6. Atomic force microscopy (AFM) images of SCS 20 nm thick a, In$_2$O$_3$, b, IZO, and c, IGZO films on SiO$_2$ annealed at the indicated temperatures.
Figure S7. Atomic force microscopy (AFM) images of 20 nm SCS In$_2$O$_3$ films scanned over the indicated areas: a, 50 µm × 50 µm, b, 10 µm × 10 µm, and c, 2 µm × 2 µm.

Figure S8. Atomic force microscopy (AFM) images of 50 nm SCS a, In$_2$O$_3$, b, IZO and c, IGZO films annealed at 300 °C.

Figure S9. Scanning electron microscopy (SEM) images of 20 nm In$_2$O$_3$, IZO, and IGZO films deposited by spin-coating (5 nm ×4 layers) and SCS at the indicated processing temperatures.
Figure S10. High angle annular dark field (HAADF) STEM images of In$_2$O$_3$ films deposited using a. spin-coating/combustion (5 nm x 4 layers), and b. deposited using SCS (20 nm) annealed at 300 °C.
Figure S11. Transfer and output plots of the spin-coated 20 nm thick oxide films at various processing temperatures (on 300 nm SiO$_2$/Si substrates): a, In$_2$O$_3$ films, b, IZO films, c, IGZO films.
Figure S12. Transfer and output plots of the SCS 20 nm thick oxide films at various processing temperatures (on 300 nm SiO$_2$/Si substrates): a, In$_2$O$_3$ films, b, IZO films, c, IGZO films.
Figure S13. Representative transfer plot for a 20 nm thick SCS IZO film on 45 nm ZrO$_2$/ITO glass substrates processed at 300 °C. The FET mobility of this device is ~ 90 cm$^2$/Vs-1.
Figure S14. Representative transfer plots for SCS (20 nm, processing at 300 °C) and sputtered IGZO TFTs.
Figure S15. Representative transfer plots for two Spray IGZO TFTs without fuel processed at 300 °C.
Figure S16. a. Characterization of 40 nm Al₂O₃ dielectric layers processed at 200 °C: C-V measurements at 10 kHz, and frequency measurements at 2 V. b, Transfer and output characteristics of the SCS flexible In₂O₃ films (on 40 nm Al₂O₃/Arylite substrates) processed at 200 °C. c, Optical image of flexible SCS In₂O₃ TFTs on an Arylite substrate (40 nm Al gate electrode/40 nm Al₂O₃ dielectric, with 40 nm Al source and drain electrodes).
Figure S17. **a. Top.** Schematic representation for a fully patterned sputtered IGZO TFT. **Bottom.** Representative I-V plots (V_D = 45 V) corresponding to a negative bias stress experiment (V_D = 10 V, V_G = -30 V, T = 60°C, 5 min cycle). **b. Top.** Schematic representation for a sputtered IGZO TFT with patterned only the IGZO layer. **Bottom.** Representative I-V plot (V_D = 45 V). **c. Top.** Schematic representation for a sputtered IGZO TFT without patterning as used in this study. **Bottom.** Representative I-V plot (V_D = 80 V). GE = gate electrode, GI = gate insulator.
Figure S18. **Top.** Schematic representation for a fully patterned sputtered IGZO TFT. **Bottom.** Representative I-V plots ($V_D = 45$ V) corresponding to a negative bias stress experiment ($V_D = 10$ V, $V_G = -30$ V, $T = 60^\circ$C, 5 min cycle). GI = gate insulator.
Figure S19. a. C-V measurements of 45 nm ZrO$_2$ dielectric layers processed at 350 °C at 10 kHz. b. Transfer and c. output characteristics of the SCS flexible IGZO111 (on 45 nm ZrO$_2$/ITO glass substrates) processed at 350 °C.
Figure S20. XRR of IGZO films with composition 1:0.11:0.29 by sol-gel and spin-SC.
Figure S21. X-ray photoelectron spectra of 50 nm thick IGZO films by various deposition methods: a, with composition (In:Ga:Zn=111, solution processed IGZOs were annealed at 350 °C). b, with composition (In:Ga:Zn= 1: 0.11: 0.29, processed at 300 °C). The table summarizes the O% from deconvolution analysis.

<table>
<thead>
<tr>
<th></th>
<th>IGZO 111</th>
<th>IGZO 1:0.11:0.29</th>
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<tbody>
<tr>
<td></td>
<td>M-O-M (%)</td>
<td>M-OH (%)</td>
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<tr>
<td>Sol-gel</td>
<td>0.31</td>
<td>0.38</td>
</tr>
<tr>
<td>Spin-CS</td>
<td>0.32</td>
<td>0.42</td>
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<tr>
<td>SCS</td>
<td>0.45</td>
<td>0.41</td>
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<tr>
<td>Sputtering</td>
<td>0.58</td>
<td>0.28</td>
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Figure S22. **a**, \( S_r \) parameter as a function of the positron implantation energy. The continuous lines are the best fits using three-layer model using VEPFIT. The vertical dashed lines mark the position of the nominal interfaces IGZO/SiO\(_2\). Error bars are shown for one point only in each evolution. **b**, Reduced chi-square statistic of the \( S_r \)-parameter (calculated for thicknesses lower than 100 nm) as a function of the number density of the IGZO films.
Figure S23. a, Energy band depth profile in IGZO TFT devices. b, Transfer $I_D$-$V_{GS}$ curves (at low $V_{DS}$ 5 V) and c, capacitance voltage C-V characteristics of sputtered and two SCS IGZO (In:Ga:Zn=111 and 1: 0.11: 0.29) films deposited on ultra-low resistivity Si ($\rho$ as small as 0.001)/CVD SiNx(200 nm)/SiOx (100 nm) substrates. TFTs: Conventional sol-gel deposited; Combustion post annealing deposited; d, Spatial profiles of surface bend bending for the corresponding IGZO films.
Table S1. Results obtained in the IGZO/SiO₂/Si heterostructure from the positron lineshape profiles (Fig. 4c) using VEPFIT. Positron diffusion length $L_+$, thickness $Z$, $S_r$-parameter and $F_{3y}$ fraction. The thickness, the positron diffusion length and the $S_r$-parameter of the SiO₂ film in all cases were: 300(8) nm, 16(2) nm and 0.981(2), respectively. The positron diffusion length in the p-Si substrate was 110(20) nm. Fixed parameters are denoted with the letter F.

<table>
<thead>
<tr>
<th>Method</th>
<th>$L_+$ (nm)</th>
<th>$Z$ (nm)</th>
<th>$S_r$-parameter</th>
<th>$F_{3y}$ %</th>
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</thead>
<tbody>
<tr>
<td>sputtered (1:1:1)</td>
<td>12(2)</td>
<td>55 F</td>
<td>0.878(1)</td>
<td>0.7(5)</td>
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<tr>
<td>sol-gel (1:1:1)</td>
<td>6(2)</td>
<td>32 F</td>
<td>0.933(1)</td>
<td>5.2(6)</td>
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<tr>
<td>spin-CS (1:1:1)</td>
<td>5(2)</td>
<td>27 F</td>
<td>0.932(1)</td>
<td>5.0(6)</td>
</tr>
<tr>
<td>SCS (1:1:1)</td>
<td>10(2)</td>
<td>50 F</td>
<td>0.904(1)</td>
<td>2.1(5)</td>
</tr>
<tr>
<td>SCS (1:0.1:0.29)</td>
<td>11(2)</td>
<td>27 F</td>
<td>0.881(1)</td>
<td>0.9(5)</td>
</tr>
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</table>

Table S2. Mass Densities of In₂O₃, Ga₂O₃, ZnO single crystal powders.

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Density (g cm⁻³)</th>
<th>Reference</th>
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<tr>
<td>In₂O₃</td>
<td>7.18</td>
<td>9-11</td>
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<tr>
<td>Ga₂O₃</td>
<td>6.44</td>
<td>12,13</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.61</td>
<td>14,15</td>
</tr>
</tbody>
</table>

Table S3. Conductivity and thickness of ITO films fabricated by the indicated methods.

<table>
<thead>
<tr>
<th>ITO films</th>
<th>Conventional sol-gel</th>
<th>Combustion spin</th>
<th>SCS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S cm⁻¹)</td>
<td>81.2±12.9</td>
<td>127.4±10.1</td>
<td>174.6±12.5</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>~105</td>
<td>~107</td>
<td>~96</td>
</tr>
</tbody>
</table>
References