Expeditious, scalable solution growth of metal oxide films by combustion blade coating for flexible electronics

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Significance

Solution-processing metal oxide (MO) films at low temperature enables their integration in mechanically flexible and inexpensive substrates for unconventional optoelectronics. However, temperature reduction has not been accompanied by a corresponding reduction in film-processing time, which remains far greater than acceptable for efficient/continuous additive manufacturing as in typical fabrication lines. Here, we report a highly efficient cofuel-assisted combustion process, which involves introducing both a fluorinated fuel and a preannealing step, that achieves ultrafast reaction and metal–oxygen–metal (M–O–M) lattice condensation within 10–60 s for several MO semiconductors and aluminum oxide dielectric. The resulting MO transistors exhibit high carrier mobility, excellent bias stability, and good flexibility.


Revisers: R.G.G., Harvard University; H.K., Max Planck Institute for Solid State Research; and T.N.N., University of California, San Diego.

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Metal oxide (MO) semiconductor thin films prepared from solution typically require multiple hours of thermal annealing to achieve optimal lattice densification, efficient charge transport, and stable device operation, presenting a major barrier to roll-to-roll manufacturing. Here, we report a highly efficient, cofuel-assisted scalable combustion blade-coating (CBC) process for MO film growth, which involves introducing both a fluorinated fuel and a preannealing step to remove deleterious organic contaminants and promote complete combustion. Ultrafast reaction and metal–oxygen–metal (M–O–M) lattice condensation then occur within 10–60 s at 200–350 °C for representative MO semiconductor [indium oxide (In2O3), indium-zinc oxide (IZO), indium-gallium-zinc oxide (IGZO)] and dielectric [aluminum oxide (Al2O3)] films. Thus, wafer-scale CBC fabrication of IGZO-Al2O3 thin-film transistors (TFTs) (60-s annealing) with field-effect mobilities as high as ~25 cm2 V−1 s−1 and negligible threshold voltage deterioration in a demanding 4,000-s bias stress test are realized. Combined with polymer dielectrics, the CBC-derived IGZO TFTs on polyimide substrates exhibit high flexibility when bent to a 3-mm radius, with performance bending stability over 1,000 cycles.

thin-film transistor | solution process | ultrashort annealing time | combustion synthesis | blade coating

The recent commercialization of metal oxide (MO) thin-film transistors (TFTs) highlights the many attractions of amorphous MOs (a-MOs) over competing semiconductor technologies (1–9). Furthermore, and in contrast to current capital-intensive vapor deposition growth, solution-processed a-MO films promise to reduce manufacturing costs (10–14) as well as enable flexible optoelectronics on inexpensive plastic substrates (15–21). This possibility reflects the substantial lowering of MO film-processing temperatures from >450–600 °C to recently as low as 150–300 °C (11, 22–29). However, this dramatic temperature reduction has not been accompanied by a corresponding reduction in film-processing time, which remains far greater than acceptable for efficient/continuous additive manufacturing as in typical fabrication lines. Here, we report a highly efficient cofuel-assisted combustion process, which involves introducing both a fluorinated fuel and a preannealing step, that achieves ultrafast reaction and metal–oxygen–metal (M–O–M) lattice condensation within 10–60 s for several MO semiconductors and aluminum oxide dielectric. The resulting MO transistors exhibit high carrier mobility, excellent bias stability, and good flexibility.

Supporting Information


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The field-effect mobilities of these CBC IGZO-Al2O3 TFTs (300 °C/60 s) are as high as 25.2 cm²V⁻¹s⁻¹ with negligible threshold voltage deterioration in a 4,000-s bias stress test. Finally, highly flexible solution-processed CBC IGZO TFTs with a top-gated polymer dielectric on polyimide (PI) films are reported.

Results

MO-Precursor Powder Analysis and Thin-Film Growth. To probe the importance of solvent removal from the MO-precursor powders/films before combustion, and that of the cofuel, we first investigated wet and dry IGZO powders as well as wet, dry, and combustion-derived IGZO films prepared with AcAcH and/or FAcAcH (see Fig. 1 and SI Appendix for details). The IGZO powder/film precursor solutions were prepared by 14 h of aging a mixture of In/Ga/Zn nitrates (1.4 mol, 1:0.1:0.3 atomic ratio) as the metal source/oxidizer, AcAcH as the fuel (1.4 mol), and FAcAcH as the cofuel (0.0 or 0.32 mol) in 2-methoxyethanol (2-ME) (SI Appendix, Fig. S1 and Table S1). Proton NMR (¹H NMR) spectroscopy (SI Appendix, Figs. S2–S9) indicates that during the IGZO solution aging, the AcAc⁻ coordinates to the metal ions, while less basic FAcAc⁻ does not but nevertheless influences the metal–AcAc coordination (11). For powder preparation, the precursor solutions were dried in a vacuum for 5 and ~30 h at 25 °C to obtain “wet” and “dry” samples, respectively (Fig. 1B). For film growth (Fig. 1C), the same solutions were spin-coated to afford wet films, while “preannealing” at 120 °C/60 s yielded dry MO-precursor films. Subsequent combustion of the wet or dry films by annealing at 200–300 °C for 10 s to 20 min afforded the corresponding MO films. Fig 1 B and C shows the process details and nomenclature. Simultaneous thermogravimetry and differential scanning calorimetry (TGA/DSC) measurements were next used to investigate residual solvent and cofuel effects on the MO thermal
and compositional evolution during combustion. TGA/DSC data (SI Appendix, Fig. S10) show that the combustion ignition temperature ($T_c$) for dry combustion synthesis (CS) IGZO and fuel-assisted CS (FA-CS) IGZO powders were 149.5 and 144.7 °C, respectively, versus 147.9 and 137.9 °C for the corresponding wet samples (SI Appendix, Table S2). The combustion heats ($\Delta H_{\text{exo}}$)/residual weights ($\text{RW}$) for the wet CS IGZO and FA-CS IGZO powder samples were 366.0 kJ g$^{-1}$/33.4% and 429.6 kJ g$^{-1}$/25.0%, respectively, compared with 640.6 kJ g$^{-1}$/42.2% and 662.8 kJ g$^{-1}$/37.1% for the corresponding dry powders. These results indicate that residual solvent significantly depresses the heat generated during combustion, a key factor in film densification and ultimate film charge-transport capacity. Furthermore, cofuel addition significantly increases the heat generated and accelerates precursor decomposition to volatile components.

Independent of the precursor composition and cofuel present, the wet films resulting from a single spin-coating step are ~20 nm thick, as determined by ellipsometry. These films contain significant quantities of solvent, metal acetylacetonate complexes, and other organic species, as determined by $^1$H NMR spectroscopy (SI Appendix, Figs. S2–S9). Preannealing the wet films at 120 °C for 60 s removes solvent and significantly densifies them, with the film thickness reduced to ~8 nm. Note that this step does not result in combustion or formation of significant metal-oxygen-metal (M-O-M) lattice condensation, as assessed by TGA/DSC and X-ray photoelectron spectroscopy (XPS) (vide infra). Subsequent CS of both wet and dry (prebaked) films at 200–300 °C for 10 s to 20 min then results in ~3-nm-thick films. For MO film analysis and TFT fabrication, the spin-coating/annealing process was repeated four times (vide infra).

XPS was next applied to characterize the oxygen-bonding states and their evolution with film processing and fuel/cofuel composition (Fig. 2A). The O(1$s$) ionization can be deconvoluted into three peaks at 529.9, 531.2, and 532.3 eV, assigned to oxygen anions in an M-O-M lattice, M-OR bonds, and M-OH species, respectively (39). Data for all samples are summarized in SI Appendix, Table S3. From the XPS data, it is clear that both the wet and dry IGZO films (Fig. 2A, B) show similar oxygen bonding states, with the wet films showing slightly lower intensities for the M-OH species.

Fig. 2. Structural/morphological properties and device performance of IGZO films/TFTs. (A) O(1$s$) X-ray photoelectron spectra and their deconvolutions in spin-coated IGZO films subjected to the indicated processing stages: As-spun (wet), preannealed (dry), CS, P-CS, and P-FA-CS. (B and C) Cross-section TEM images of four-layer spin-coated IGZO films processed by CS (B) and P-CS (C) methods. (D) Transfer plots of 300 °C-processed IGZO TFTs on 300-nm SiO$_2$/Si substrates processed by CS, P-CS, and P-FA-CS methods. (E) 3D plot of mobility-total annealing time-deposition process for IGZO TFTs on 300-nm SiO$_2$/Si substrates.
do not contain significant densities of M-O-M species; however, the latter films have higher M-O content (40.5% vs. 30.2%), consistent with more extensive acetylacetonate coordination and film densification on solvent removal. These data also confirm that negligible combustion occurs during the spin-coating/preannealing steps. Remarkably, comparing the XPS data for the wet film without cofuel heated at 300 °C for 20 min, which corresponds to the conventional combustion process for CS IGZO films (11, 15), to that obtained by annealing the dry film for 10 s in the present process to yield preannealing CS (P-CS) IGZO films, reveals that substantial/comparable M-O-M lattice formation occurs (74.5% vs. 75.0%, respectively) despite a >100× reduction in annealing time. Furthermore, using the fluorocarbont cofuel with preannealing (samples P-FA-CS IGZO) additionally densifies the IGZO films to a 75.9% M-O-M content. Top-view and crosssection transmission electron microscopy (TEM) of the IGZO films (Fig. 2 B and C and SI Appendix, Figs. S11–S12) fabricated by CS and P-CS further confirm the superior quality of the latter, which are denser and more uniform, in contrast to the multilayer morphology of the conventional CS sample. Finally, grazing incidence X-ray diffraction (GIXRD) film scans (SI Appendix, Fig. S13) indicate that the CS, P-CS, and P-FA-CS derived IGZO (300 °C/60 s) films remain amorphous.

IGZO TFTs. Next, the performance of IGZO TFTs on 300-nm SiO2/Si dielectric/substrate [Al source-drain contacts; width/length (W/L) = 1,000/100 μm] fabricated using the different processing methods (CS, FA-CS, P-CS, P-FA-CS) and combustion temperatures/times are compared and contrasted. Fig. 2D and SI Appendix, Fig. S14 show representative TFT transfer and output characteristics. The device statistics are summarized in Fig. 2E and SI Appendix, Tables S1 and S4. The P-CS and P-FA-CS IGZO TFTs begin to function at 200 °C/20 min processing with average mobilities (μ) of 0.08 and 0.1 cm2 V−1 s−1, respectively, while all TFTs fabricated by the other methods are inactive. After 225 °C/20-min annealing, the μ of the IGZO TFTs increases from 0.17 cm2 V−1 s−1 (CS) to 0.78/0.92 cm2 V−1 s−1 (P-CS/P-FA-CS). These values are unprecedented for solution-processed IGZO TFTs at such a low temperature. As shown in Table 1, when the annealing temperature is further increased to 250 °C and then to 300 °C, the mobility increases dramatically even for the rather short annealing times (10–60 s). For example, the mobilities of the P-CS and P-FA-CS IGZO TFTs annealed at 300 °C for 10 s are 1.60 and 2.05 cm2 V−1 s−1, compared with only 0.19 cm2 V−1 s−1 for CS-derived IGZO TFTs. Annealing at the same temperature for 60 s further increases μ of the P-FA-CS devices to 5.44 cm2 V−1 s−1, even larger than that of CS IGZO film annealed for 20 min (4.2 cm2 V−1 s−1) and >10x greater than that of CS IGZO annealed for 60 s (0.41 cm2 V−1 s−1). Note that the control IGZO TFTs fabricated by sol–gel exhibit far lower performance, demonstrating that the present strategy is only applicable to combustion-derived formulations (SI Appendix, Fig. S14 and Table S5). Having the mobility data for IGZO TFTs fabricated at different temperatures and annealing times shows that there is a tradeoff between the annealing temperature and annealing time to achieve a specific mobility. For instance, SI Appendix, Fig. S14I shows the P-FA-CS IGZO TFTs with electron mobilities of 1 cm2 V−1 s−1 fabricated at different temperatures and annealing times for each layer, which follows an exponential relationship.

Scope: Other MO Thin-Film Materials and Transistor-Structure Performance Correlations. Considering the excellent results achieved for the P-FA-CS IGZO films discussed above, the scope of this study was expanded to other important MO semiconductors such as binary InO3 and ternary IZO films. Comparative XPS analysis (Fig. 3 A and SI Appendix, Fig. S15) indicates that, in all cases, using the P-CS and P-FA-CS processing enhances M-O-M content by ~2–3%. For instance, 300 °C/10-s processed InO3 and IZO M-O-M content increases going from CS (71.5 and 71.9%, respectively) to P-CS (74.1 and 73.4%, respectively) to P-FA-CS (74.5 and 74.0%, respectively) processed films. Interestingly, although the carrier mobilities of the InO3 and IZO TFTs are greater than those of corresponding IGZO TFTs (vide infra), the M-O-M ratios are smaller than those of the IGZO films, reflecting strong Ga oxygen “getter” effects (37). Next, the performance of InO3 and IZO TFTs are compared in Fig. 3B, Tables 1 and SI Appendix, Figs. S16–S17 and Table S4. No TFT response is observed for 200 °C/20 min-processed CS InO3 TFTs, while μ of the 225 °C/20 min-processed CS-InO3 TFTs is 0.21 cm2 V−1 s−1. In contrast, P-CS InO3 TFTs begin to function on annealing at 200 °C/20 min with μ = 0.075 cm2 V−1 s−1, increasing to ~3 cm2 V−1 s−1 at 225 °C/20 min. On annealing at 250 °C for 60 s, the μ of the InO3 TFTs increases from CS (0.50 cm2 V−1 s−1) to P-CS (2.94 cm2 V−1 s−1). The μ of the P-CS InO3 TFTs further increases to 9.60 cm2 V−1 s−1 after 250 °C/20-min annealing, vs. 2.06 cm2 V−1 s−1 for CS InO3 TFTs. When the InO3 films are annealed at 300 °C for only 10 s, high mobilities of 5.20 cm2 V−1 s−1 (P-CS) and 6.52 cm2 V−1 s−1 (P-FA-CS) are achieved, vs. 1.25 cm2 V−1 s−1 for CS InO3 TFTs. For IZO TFTs, CS films and P-CS films annealed at 225 °C/20 min exhibit μ = 0.04 and 0.5 cm2 V−1 s−1, respectively. When processed at 250 °C/60 s, the P-CS films exhibit a μ = 2.34 cm2 V−1 s−1, ~8.5x higher than that of the CS-IZO TFTs (0.33 cm2 V−1 s−1). For 300 °C/10-s annealing, the CS-IZO TFTs exhibit a μ = 0.31 cm2 V−1 s−1, considerably lower than those of P-CS, 2.37 cm2 V−1 s−1 and P-FA-CS, 3.78 cm2 V−1 s−1 processed devices.

To better understand the origin of the impressive P-FA-CS IGZO TFT performance, X-ray reflectivity (XRR) measurements were performed on the IGZO channel layer (SI Appendix, Materials and Methods).
and SI Appendix The morphological and microscopic requirements for TFT dielectric layers are even more stringent than for semiconducting layers, to ensure low leakage currents, high breakdown voltages, high capacitances, and minimal bulk/interface trap densities. Thus, harsh processing conditions (>450 °C/1 h) and/or significant film thicknesses (≥100 nm) are typically required for high-performance solution-processed MO dielectric films (10, 39, 41–43). Here, we show that the present processing method yields high-quality Al2O3 dielectric films for low-voltage MO TFT operation. Thus, the Al2O3 precursors Al(NO3)3 and AcAcH NH2OH in 2-ME with or without FacAcH as a cofuel were spin-coated onto n++ Si substrates and subsequently preannealed at 120 °C for 60 s, then immediately annealed at 350 °C for 60 s. This process was repeated four times to achieve the desired film thickness. Fig. 3E details the insulating properties of the CS, FA-CS, P-CS, and P-FA-CS processed Al2O3 dielectrics (~20 nm thick), indicating that the CS Al2O3 film leakage current density (4.1 × 10−6 A cm−2) at 1 MV cm−1 and the BF (1.9 MV cm−1) are inferior to those of P-SC Al2O3 (1.1 × 10−7 A cm−2 and 2.8 MV cm−1, respectively) and especially P-FA-CS Al2O3 (7.5 × 10−8 A cm−1 and 3.2 MV cm−1) films. SI Appendix, Fig. S19 provides the frequency- and voltage-dependent capacitance per unit area of the aforementioned dielectrics, and the corresponding dielectric constants are shown in Fig. 3F. The CS-Al2O3 films exhibit the largest dielectric constant (k = 9.4), likely reflecting impurities and large densities of polar hydroxyl groups (39), as well as a pronounced fall in capacitance for frequencies >7 × 105 Hz. In contrast, the P-CS and P-FA-CS-Al2O3 films exhibit frequency-stable capacitances of 317 nF cm−2 for P-CS and 286 nF cm−2 for P-FA-CS up to 4 × 105 and 5 × 105 Hz, respectively, and dielectric constants of 7.9 and 7.3, respectively. That the lower dielectric constant of these films is due to lowered impurities and fluoride incorporation (AlF3, k = 2.2) is supported by XPS data, which indicate Al-F features at 685.6 eV (SI Appendix, Fig. S20) (44). From deconvolution, the estimated atomic F/Al ratios for the CS and P-FA-CS-Al2O3 films are 1:13.9 and 1:10.8, respectively. Note that no F incorporation is observed by XPS in the FAcAcH-prebaking approach applied to MO films, even though the annealing temperature is 50–100 °C lower than that for the Al2O3 films (SI Appendix, Fig. S20). This result likely reflects the very strong Al-F bond energy (675 kJ mol−1) versus that of the other metal fluorides: In-F, 516 kJ mol−1; Ga-F, 584 kJ mol−1; and Zn-F, 364 kJ mol−1 (45). Regarding the oxygen environment (SI Appendix, Fig. S21), the deconvoluted XPS O(1s) spectra assign Al-O-Al at 531.1 ± 0.1 eV and O-associated hydroxyl groups at 532.3 ± 0.1 eV (46, 47). The Al-O-Al content increases from 59.5% (CS) to 77.5% (FA-CS) to 80.0% (P-CS) to 82.6% (P-FA-CS), again demonstrating that the cofuel/prebaking approach accelerates MO dielectric oxide lattice densification.

Printed MO Films and Devices. Blade coating (BC) was next applied to MO film growth using the present processing methodology as...
CBC. CBC has advantages over spin-coating, including concurrent preannealing during film deposition, minimal precursor solution wastage (reduced by \(\sim 10 \times\)), and scalability (48). Critical deposition parameters including coating speed (5–20 mm s\(^{-1}\)), gap height (100/300 \(\mu\)m), and substrate temperature (room temperature/70 °C) were optimized to balance metal ion-AcAc\(^{-}\)/FAcAc\(^{-}\) coordination, solvent evaporation, solution flow thermodynamics, and desired final film thickness (SI Appendix, Table S22 and Table S6). CBC of the IGZO semiconductor layer on Si/SiO\(_2\) substrates was first optimized, yielding the parameters: 10 mm s\(^{-1}\) coating speed, 100-\(\mu\)m gap height, 70 °C substrate temperature, and four successive coatings for \(\sim 6\)-nm-thick films.

Fig. 4A, Table 2, and SI Appendix, Table S6 summarize device metrics for the IGZO films processed by different methods. Thus, while the \(\mu\) of spin-coated CS IGZO TFTs annealed at 250 °C/60 s is only 0.10 cm\(^2\) V\(^{-1}\) s\(^{-1}\) (vide supra), the BC/CS and BC/FA-CS devices exhibit mobilities of 0.26 and 0.96 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively. By raising the temperature to 300 °C, the BC/FA-CS IGZO TFT mobilities reach 3.74 cm\(^2\) V\(^{-1}\) s\(^{-1}\) (10-s annealing) and 7.66 cm\(^2\) V\(^{-1}\) s\(^{-1}\) (60-s annealing), which are significantly larger than obtainable by spin-coating the IGZO layer (2.05 and 5.44 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively). This result may reflect more efficient preannealing, which occurs immediately after dispensing the IGZO-precursor solution.

Table 2. Performance metrics of IGZO TFTs on 300 nm SiO\(_2\)/Si substrates processed by various combustion methods

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Performance parameters</th>
<th>250 °C/60 s</th>
<th>300 °C/10 s</th>
<th>300 °C/60 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC/CS</td>
<td>(\mu) (cm(^2) V(^{-1}) s(^{-1}))</td>
<td>0.26 ± 0.05</td>
<td>0.62 ± 0.05</td>
<td>4.53 ± 0.67</td>
</tr>
<tr>
<td></td>
<td>(V_T) (V)</td>
<td>24.1 ± 4.79</td>
<td>4.55 ± 1.59</td>
<td>9.78 ± 0.99</td>
</tr>
<tr>
<td></td>
<td>(I_{on}/I_{off})</td>
<td>(\sim 10^4)</td>
<td>(\sim 10^6)</td>
<td>(\sim 10^6)</td>
</tr>
<tr>
<td>BC/FA-CS</td>
<td>(\mu) (cm(^2) V(^{-1}) s(^{-1}))</td>
<td>0.96 ± 0.12</td>
<td>3.74 ± 0.23</td>
<td>7.66 ± 0.60</td>
</tr>
<tr>
<td></td>
<td>(V_T) (V)</td>
<td>20.1 ± 6.71</td>
<td>22.54 ± 0.97</td>
<td>15.82 ± 0.42</td>
</tr>
<tr>
<td></td>
<td>(I_{on}/I_{off})</td>
<td>(\sim 10^7)</td>
<td>(\sim 10^7)</td>
<td>(\sim 10^6)</td>
</tr>
</tbody>
</table>

Fig. 4C and SI Appendix, Table S6 summarize IGZO TFT performance on 300-nm SiO\(_2\)/Si substrates (source/drain = Al; W/L = 1,000/100 \(\mu\)m) versus that of the recent literature report, clearly demonstrating the technological attractions of BC/FA-CS methodology. Positive gate-bias stress (PTBS) measurements were also carried out on the 60 s-annealed P-FA-CS and BC/FA-CS IGZO TFTs (Fig. 4D and SI Appendix, Fig. S24). These devices were subjected to a constant \(V_{GS}\) of +20 V for up to 2,000 s (400-s intervals) in ambient, without encapsulation or back channel protection. The P-FA-CS IGZO devices exhibit \(\Delta V_T\) of \(\sim 4-9\) V after 2,000 s, implying a large density of acceptor-like electron-trapping states (11, 17, 49).
However, no obvious shift is observed for BC/FA-CS IGZO TFTs even after a gate-bias stress time of 2,000 s with $\Delta V_T \sim \pm 2\ V$.

Next, BC $\text{Al}_2\text{O}_3$ dielectric films and BC IGZO/$\text{Al}_2\text{O}_3$ TFTs were fabricated to further demonstrate the technological advances provided here. BC/FA-CS $\text{Al}_2\text{O}_3$ fabrication process parameters are identical to those of IGZO films, except that the gap height is 300 $\mu\text{m}$. Fig. 4B shows the variations in leakage current densities for 350 $^\circ\text{C}/60$ s-annealed $\text{Al}_2\text{O}_3$ films at different electric field strengths, and SI Appendix, Fig. S25 shows the electrical and dielectric properties. Remarkably, the BC/FA-CS $\text{Al}_2\text{O}_3$ films, $\sim 15$ nm thick after four sequential coatings, exhibit excellent dielectric characteristics, again with the performance of the processed films ($J = 8.1 \times 10^{-8}$ A cm$^{-2}$ at 2.0 MV; $\text{BF} = 7.2$ MV cm$^{-1}$) outperforming the BC/CS ones ($J = 4.3 \times 10^{-7}$ A cm$^{-2}$ and $\text{BF} = 6.5$ MV cm$^{-1}$). Both films exhibit frequency-stable capacitance up to $5 \times 10^5$ Hz, and their dielectric constants are 6.8 and 6.6, respectively. Fig. 5A and B and Movie S1 show the BC/FA-CS IGZO/$\text{Al}_2\text{O}_3$ device fabrication process on a 4-inch-diameter Si substrate and the optical image of a low-voltage IGZO-$\text{Al}_2\text{O}_3$ TFT with patterned IGZO and S/D.
layers. These devices exhibit excellent TFT characteristics at low voltage (≤2 V), negligible I-V hysteresis (Fig. 5C), and field-effect mobilities centered at ~18.0 cm^2 V^-1 s^-1 (maximum value = 25.2 cm^2 V^-1 s^-1) with an SD of ±2.5 cm^2 V^-1 s^-1 over 100 devices (Fig. 5D and SI Appendix, Fig. S26). These TFTs also exhibit excellent current on/off modulation, subthreshold swing, and threshold voltage (V_T) values of >4 × 10^3 V dec^-1, and 0.55 ± 0.27 V, respectively, as well as a negligible ΔV_T of ±0.06 V after 4,000 s stress time (Fig. 5E and SI Appendix, Fig. S27).

Finally, top-gate, top-contact IGZO TFTs were fabricated on a ~25-μm, 35-μm-thick PI substrate with a polymer dielectric (Actenvik D3300; Flexterra Corporation) and a CBC IGZO layer annealed for only 60 s at 300 °C (Fig. 5F). Fig. 5G shows the transfer plots of these devices at various bending radii about a curvature parallel to the channel length. These devices exhibit only a slight turn-on voltage (V_on) shift from +0.1/20.1 to 0/0.21 V as the bending radius is decreased from ∞ to 3 mm, along with a negligible mobility decline from 0.45 to 0.43 cm^2 V^-1 s^-1. The lower mobility of these devices compared with that achieved with SiO₂ reflects the difference in device architecture and the lower dielectric constant of polymer dielectric (50). Importantly, these TFTs exhibit excellent mechanical flexibility with negligible performance loss on bending at 6 mm for 1,000 times (Fig. 5H and SI Appendix, Fig. S28).

Conclusions
Low-temperature, wafer-scale fabrication of MO films via ultrasonic combustion BC is reported. Using a fluorinated cofoil to promote metal coordination and impurity removal, combined with a precursor preannealing step to eliminate solvent, greatly enhances the efficiency of CS, which can be reduced to times as short as 10 s at temperatures as low as 200–300 °C. Thus, functional (μ > 1 cm^2 V^-1 s^-1) MO TFTs are obtained at temperatures/times as low as 250 °C/60 s and/or 300 °C/10 s for InO₂, IZO, and IGZO. This approach is also extendable to MO dielectrics such as Al₂O₃. Additionally, ultrasonication of blade-coated IGZO and Al₂O₃ films yields excellent semiconductor and insulating characteristics and produces low-temperature wafer-scale MO TFTs with highly stable characteristics and ΔV_T < 0.06 V under 4,000 s bias stress. Using a polymeric top-gated dielectric on PI film then yields highly flexible, solution-processed CBC/IGZO TFTs. We anticipate that these results will help advance low-cost, high-performance, roll-to-roll compatible large-area printed electronics as well as other technologies where high-quality MO films are essential components.

Methods
Precursor Preparation and Characterization. All combustion precursor materials were purchased from Sigma-Aldrich and stored in a vacuum desiccator. First, measured quantities of the metal salts were dissolved in 5.0 mL of 2-ME. Thus, 75.2 mg of In(NO₃)₃ was used for the InO₂ precursor; 60.16 mg of In(NO₃)₃ and 9.47 mg of Zn(NO₃)₂ were used for the IZO precursor; 63.36 mg of In(NO₃)₃, 10.74 mg of Zn(NO₃)₂, and 5.38 mg of Ga(NO₃)₃ were used for the IGZO precursor; and 93.78 mg of Al(NO₃)₃ was used for the Al₂O₃ precursor. Next, 25 μL of acetylacetone and 11.25 μL of 14.5 M NH₄OH(aq) were added in sequence to each metal nitrate precursor, except that 75.0 μL of acetylacetone and 33.75 μL of 14.5 M NH₄OH(aq) were added to the In(NO₃)₃ precursor. The solutions were then stirred overnight (~14 h) before film fabrication. For fuel-assisted combustion precursors, 1,1,1-trifluro-2,4-pentanone (10 wt % to the total weight of metal nitrates) was added to the above precursor solutions 1 h before spin-coating/BC. Wet and dried precursors were obtained by vacuum evaporation using Schlenk line for 5 and 30 h, respectively. Both DSC and TGA measurements were performed on a SDT Q600 instrument (TA Instruments, Inc.). The experiments were carried out on ~1 mg of wet or dry samples with a heating rate of 10 °C min^-1 under a 70 mL min^-1 N₂ flow. Vacuum-dried precursors in anhydrous dimethyl sulfoxide-d₆ were used for ¹H NMR spectroscopic analysis. Spectra were recorded on a Bruker Avance III 500-MHz spectrometer.

Metal Oxide Thin-Film and Device Fabrication. All of the solutions were filtered through 0.2-μm syringe filters before fabrication. n- type silicon wafers with/without 300-nm SiO₂ (W250) substrates were solution-cast cleaned and then cleaned with an oxygen plasma for 5 min before use. For spin-coating fabrication, the InO₂, IZO, IGZO, and Al₂O₃ precursors were spin-coated on the substrates (n- Si, 300 nm SiO₂/Si) at 3,500 rpm for 30 s in a controlled atmosphere box (relative humidity (RH) ~ 20%) and optionally preannealed at 120 °C for 60 s (RH ~ 35%). Then, the resulting films were immediately placed on a 200–390 °C hotplate and annealed for 10 s to 20 min (RH ~ 35%). This process was repeated four times to obtain the desired film thickness. For BC film fabrication, first, the substrate (n- Si or 300 nm SiO₂/n- Si) was placed on the blade-coater (Erichsen Coater G100) setup on a surface maintained at a temperature of 25–70 °C. Next, the blade was approached to the substrates maintaining a gap of 100–300 μm. After that, the precursor solution (10 μL for 1 inch x 1 inch square substrate, 80 μL for a 4-inch-diameter substrate) was injected at the interface between the substrate and the blade until a meniscus formed. The blade was horizontally transported at a constant velocity of 5–20 mm s^-1, and the carried solution dried at a rate depending on the substrate temperature. Finally, the film was annealed at 250–350 °C for 10–60 s. This process was repeated four times to obtain the desired film thickness. Semiconductor layer patterning was achieved by spin-coating/masking/annealing. First, 150 and 100 μL of MO precursor solutions were spin-coated/annealed MO films on single-crystal NaCl, which was then dissolved in water and transferred onto Cu grids. The Cs-TEM samples were prepared directly from actual TFT devices with standard focused ion-beam milling techniques (FEI Helios NanoLab 600). A ~2-μm-thick platinum layer was deposited before the ion milling to protect samples from ion-beam damage. Electrical characterization of semiconductors was performed using MO TFT devices. Electrical characterization of dielectrics was performed using metal–insulator–metal devices. n- Si wafers with 1.5-μm natural SiO₂ layer were used as substrates, and then MO dielectrics were deposited by spin-coating or blade-coating on them. After that, top electrodes (Al, 40 nm) were thermally evaporated with size of 200 μm × 200 μm. Both the dielectrics and MO TFT measurements were performed under ambient conditions using an Agilent B1500A semiconductor parameter analyzer. The carrier mobility (μ) was evaluated in the saturation region. The areal capacitance for 300 nm SiO₂/Si is taken as 11 nf cm^-2 here. The areal capacitances of high-k Al₂O₃ and low-k polymer dielectrics (C_areal) were calculated based on the equation 1/C_areal = 1/C_areal + 1/C_DIELECTRIC, assuming that the areal capacitance of native silicon oxide (1.5 nm) is 2.3036 nf cm^-2 (39). The C_areal is the measured areal capacitance for dielectric films on 1.5 nm SiO₂/Si wafer.

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