

Supplementary Information

Polymeric Mold Soft-Patterned Metal Oxide Field-Effect Transistors: Critical Factors Determining Device Performance

Experimental Details

Materials. All reagents, zinc nitrate hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 99.9%), zinc acetylacetonate hydrate ($\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O}$, 99.9%), zinc acetate dihydrate ($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, 98%), tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99.9\%$), indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, 99.9%), and gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, 99.9%), formamide (HCONH_2 , $>99.5\%$), monoethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, 99%), ammonium nitrate (NH_4NO_3 , 99.9%), and 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, anhydrous, 99.8%) were purchased from Aldrich and used without additional purification.

Preparation of MS-ZTO, CC-ZTO, CA-ZTO, and IGZO Precursor Solutions. For the MS-ZTO precursor solution, 0.1 M metal precursor solutions were prepared using the zinc nitrate hydrate and the tin chloride dihydrate with a molar composition of Zn:Sn=1:1 in the mixture of 2-methoxyethanol, monoethanolamine, and H_2O . The molar concentration of monoethanolamine and H_2O were 0.3 and 0.2 M, respectively. For the CC-ZTO precursor solution, the tin chloride dihydrate was dissolved with ammonium nitrate in a solvent, 2-methoxyethanol, and then the zinc acetylacetonate was added with a molar composition of Zn:Sn=1:1. The molar concentration of both precursors was 0.1 M. For the CA-ZTO precursor solution, 0.1 M precursor solutions were prepared using the zinc nitrate hydrate and tin chloride dihydrate with a molar composition of Zn:Sn=1:1 in the mixture of 2-methoxyethanol, formamide, monoethanolamine, and H_2O . The 2 vol% formamide, with

respect to 2-methoxyethanol, was added, and the molar concentration of monoethanolamine and H₂O were 0.3 and 0.2 M, respectively. For the IGZO precursor solution, 0.375 M metal precursor solution was prepared using zinc acetate dihydrate, indium nitrate hydrate, and gallium nitrate hydrate in the mixture of 2-methoxyethanol, monoethanolamine, and H₂O. The chemical composition ratio of IGZO precursor solution was In:Ga:Zn = 63:10:27. All of the prepared clear solutions were stirred overnight at room temperature prior to either spin coating or MIMIC soft patterning. For reproducible experiments, the procedures of preparing precursor solutions were carried out in an Ar-filled glove box. As a control sample, all of the ZTO, and IGZO precursor solutions were spin-coated at 4000 rpm for 35 sec on 100 nm-thick SiO₂/n⁺-Si substrate, after cleaning the substrates by the following procedures: sonication with absolute ethanol, drying with an N₂ stream, and UV/O₃ treatment for 5 min. MS-ZTO, CA-ZTO, and IGZO layers were annealed at 400 °C for 2 hr in air, and the CC-ZTO layer was annealed at 350 °C for 2 hr in air.

MIMIC Soft-Patterning Process. Micrometer-sized ZTO stripe patterns were fabricated on 100 nm-thick SiO₂/n⁺-Si substrate by using MIMIC technology. The pre-patterned photoresist master molds were fabricated with a standard photolithography technique. The width was 5 μm with a spacing equal to each width and the height of 1 μm was determined by the thickness of the photoresist. Elastomeric polymer molds were fabricated by curing a mixture of PDMS precursor and curing agent (Sylgard 184, Dow Corning Corp.) with a ratio of 10:1 (w/w). The fabricated PDMS molds were placed in conformal contact with the surface cleaned SiO₂/n⁺-Si substrates to form micrometer-sized channels on the surface. Three kinds of 0.1 M ZTO precursor solutions were dropped at one end of the channels and allowed to infiltrate the channels by a capillary action. After complete evaporation of solvent, 2-methoxyethanol, at 60°C for 5 min, the PDMS mold was carefully removed to leave ZTO

stripe patterns on substrates. Then, the MS-ZTO and the CA-ZTO layers were annealed at 400 °C for 2 hr in air, and the CC-ZTO layer was annealed at 350 °C for 2 hr in air.

Device Fabrication. To fabricate TFTs with the device architecture of bottom gate/top contact, 50 nm-thick source/drain Al electrodes were deposited by thermal evaporation through a shadow mask onto the semiconductor layers. The channel dimensions in the shadow masks were 100 μm in length and 1000 μm in width, and 200 μm in length and 2000 μm in width for spin-coated and soft-patterned ZTO devices, respectively. In extracting the field-effect mobility for soft-patterned ZTO devices, the channel width was corrected by an effective dimension of ZTO layers. The transfer and output characteristics of devices were measured with an Agilent E5272 semiconductor parameter analyzer. All electrical measurements were performed in the dark under ambient conditions.

Characterization. The morphologies of patterned ZTO structures were observed using an optical microscope (Eclipse 50i-POL, Nikon), atomic force microscope (Multimode-8, Bruker), and scanning electron microscope (JSM-6700, JEOL). The chemical structures of oxide semiconductors were examined by X-ray photoelectron spectroscopy (ESCA Probe, Omicron). The surface XPS data were collected using monochromatic AlK α radiation (1486.6 eV) in an ultrahigh vacuum system with a base pressure of $\sim 10^{-10}$ Torr. The cross-sectional structures of ZTO layers were observed by a transmission electron microscope (JEM-4010, JEOL), and the viscosity of ZTO precursor solutions was monitored using a Rheometer (MCR101, Anton Parr).

Table S1. Device performance parameters for TFTs employing MS-, CA-, CC-ZTO, and IGZO channel layers prepared by different annealing methods: the ramping annealing with a heating rate of 5 °C/min and the instant annealing on preheated hotplates

Semiconductors		mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_T (V)
MS-ZTO	ramping annealing	0.005	-21.5
CC-ZTO		0.3	-12.4
CA-ZTO		0.0007	-39
IGZO		0.06	9.8
MS-ZTO	instant annealing	4.1	-0.8
CC-ZTO		7.4	3.4
CA-ZTO		7.6	3.3
IGZO		2.4	4.5

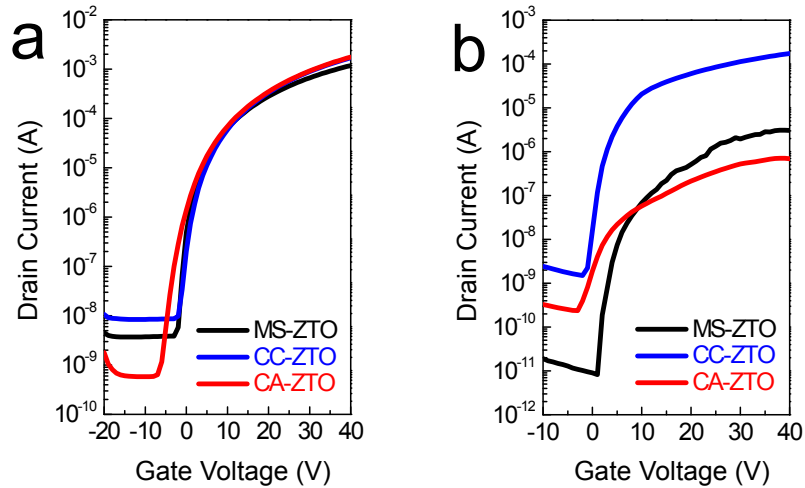


Figure S1. Transfer characteristics for TFTs employing MS-, CC-, CA-ZTO channel layers prepared by different annealing methods: (a) the instant annealing on preheated hotplates and (b) the ramping annealing with a heating rate of 5 °C/min.

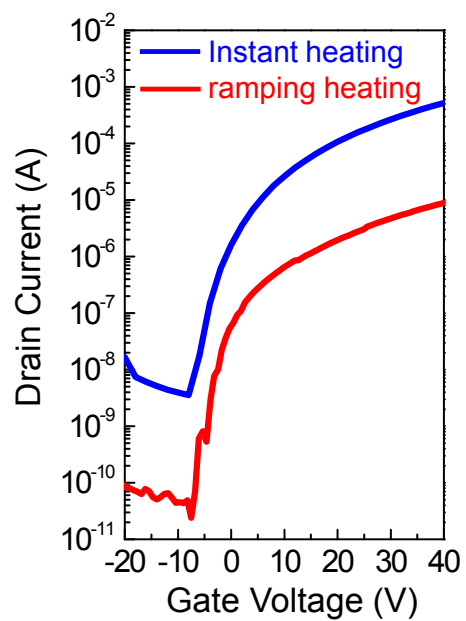


Figure S2. Transfer characteristics for TFTs employing IGZO channel layers prepared by different annealing methods: the instant annealing and the ramping annealing with a heating rate of 5 °C/min.

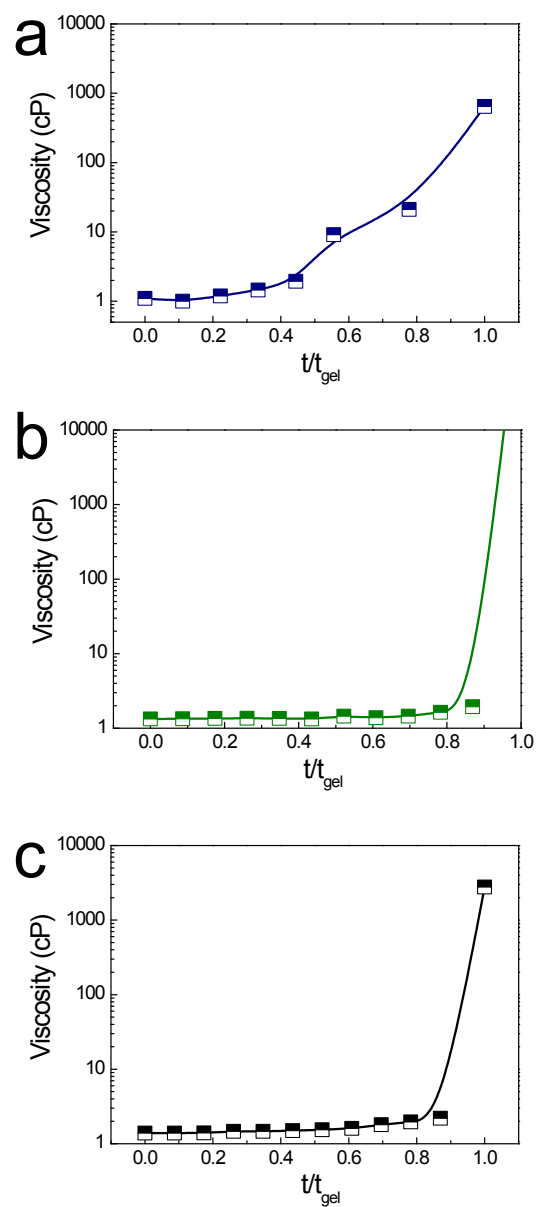


Figure S3. The viscosity variations of (a) MS-ZTO, (b) CC-ZTO, and (c) CA-ZTO precursor solutions as a function of drying time at 60 °C.