

Supplementary Information

Independent Chemical/Physical Role of Combustive Exothermic Heat in Solution-Processed Metal Oxide Semiconductors for Thin-Film Transistors

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Experimental Details

Preparation of ZTO Precursor Solution and Device Fabrication. All reagents, zinc acetylacetonate hydrate ($\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{O}$, 99.9%), tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99.9\%$), 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. For preparation of ZTO precursor solutions, 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 $\text{Zn}:\text{Sn}=1:1$. The molar concentration of both precursors was 0.1 M. The molar ratio of ammonium nitrate to zinc acetylacetonate was denoted as R, and R values were varied from 0 to 3. All of the prepared clear solutions were stirred overnight at room temperature prior to spin coating. For reproducible experiments, the procedures for preparing the precursor solutions were carried out in an Ar-filled glove box. The ZTO precursor solutions were spin-coated in air at 4000 rpm for 35 sec on 100 nm-thick $\text{SiO}_2/\text{n}^+\text{-Si}$ substrates, after the substrates were cleaned by the following procedures: sonication with absolute ethanol, drying with an N_2 stream, and UV/ O_3 treatment for 5 min. The resulting ZTO layers were pre-baked at 150 °C for 5 min and annealed at 350 °C for 2 hr in air. With the single coating process, followed by a thermal heat-treatment at 350 °C, 8 nm-thick ZTO films were obtained. 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. The transfer and output characteristics of the devices were measured with an Agilent E5272 semiconductor parameter analyzer. All electrical measurements were performed in the dark under ambient conditions.

Characterization. The chemical structures of the oxide semiconductors were examined by X-ray photoelectron spectroscopy (XPS, 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. For acquiring the compositional information from XPS spectra, we used the sensitivity factors of 28.7 and 25.0 for Zn 2p and Sn 3d, respectively. The crystal structures were analyzed with grazing angle X-ray diffraction (XRD) using CuK α radiation on a Rigaku ATX-G thin-film diffraction workstation. The surface morphologies were observed by atomic force microscope (AFM, Digital Instruments, Nano Scope IV). The cross-sectional structures were observed by a high resolution transmission electron microscope (HRTEM, JEM-4010, JEOL), and the thermal behavior was monitored using a differential scanning calorimetry (DSC, SDT Q600, TA Instruments). Optical properties were investigated by spectroscopic ellipsometry (SE, J.A. Woollam, V-VASE). X-ray absorption spectroscopy was measured by a total electron yield mode using a coherent X-ray beam source at the Pohang Accelerator Laboratory (PAL) on beam line 10D.

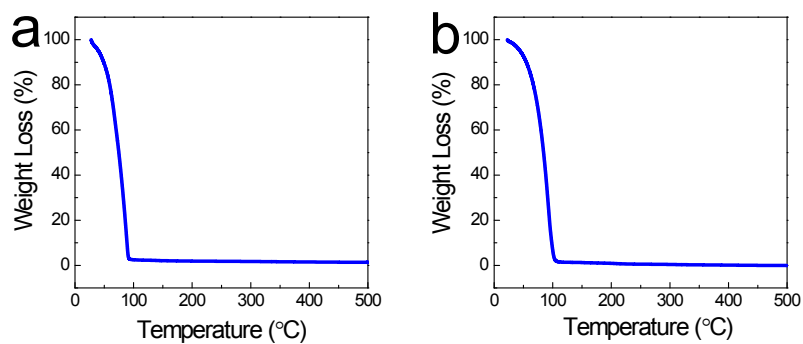


Figure S1. TGA results for R1- and R2-ZTO precursor solutions.

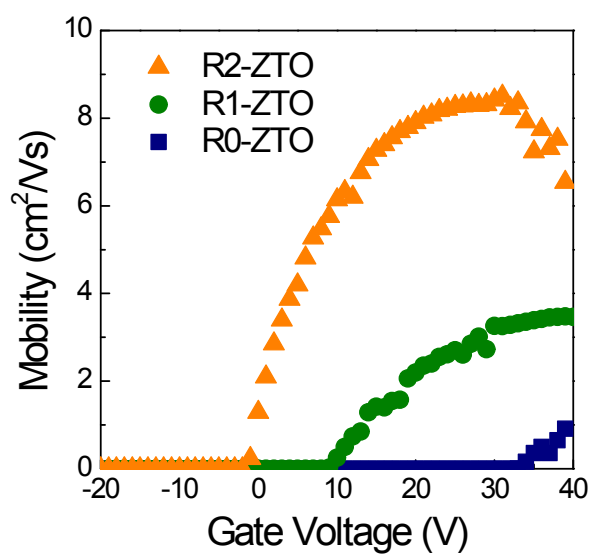


Figure S2. The variations of saturation mobilities as a function of gate voltage for all ZTO devices. The drain voltage of 40 V was applied in measuring the transfer characteristics.

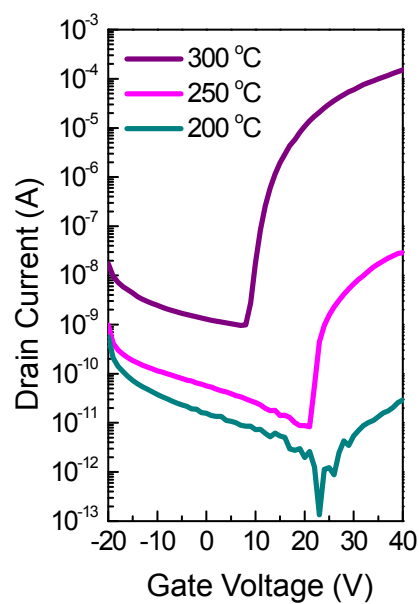


Figure S3. Transfer characteristics of R2-ZTO TFTs employing the channel layers annealed at different temperatures. The mobility and threshold voltage for TFTs with the channel layer annealed at 300 and 250 °C were 1.2 cm²/V·s and 12.3 V, and 0.0005 cm²/V·s and 19.5 V, respectively. When the channel layer was annealed at 200 °C, the device was almost inactive.

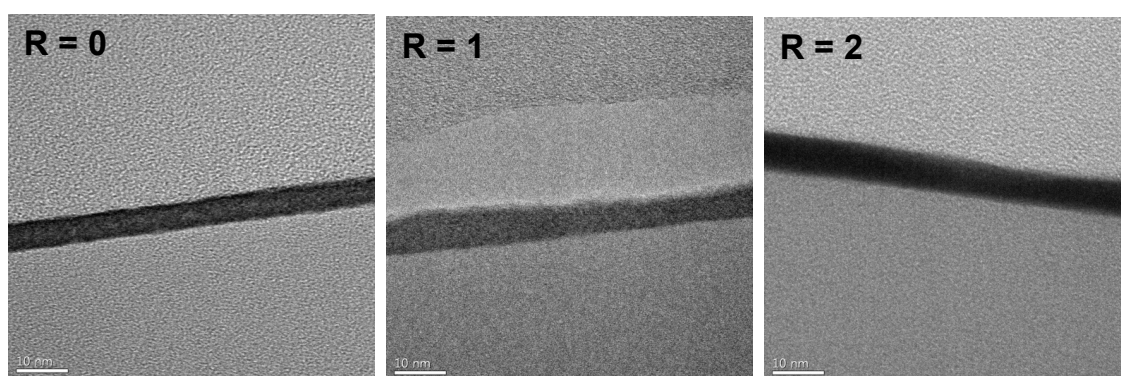


Figure S4. HRTEM images for ZTO channel layers from precursor solutions with R values of 0, 1, and 2. The molar ratio of Zn to Sn was 1.

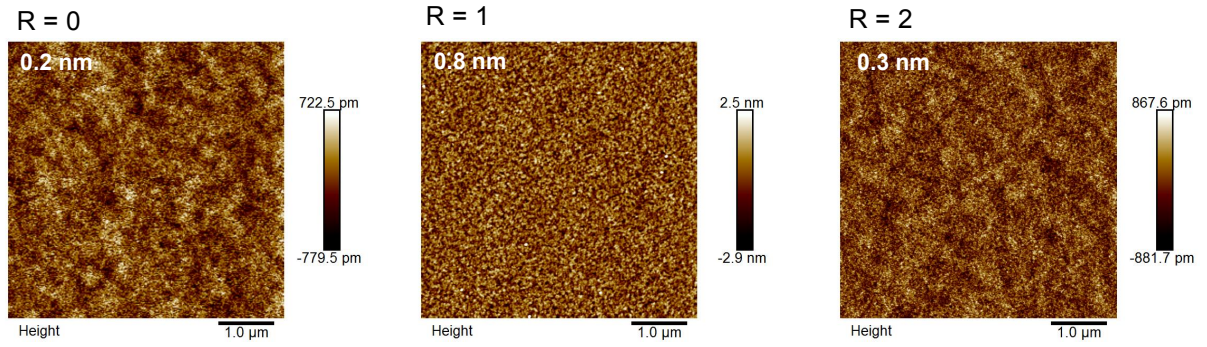


Figure S5. AFM images for ZTO channel layers from precursor solutions with R values of 0, 1, and 2. The molar ratio of Zn to Sn was 1. The numbers in the images indicate the surface roughness.

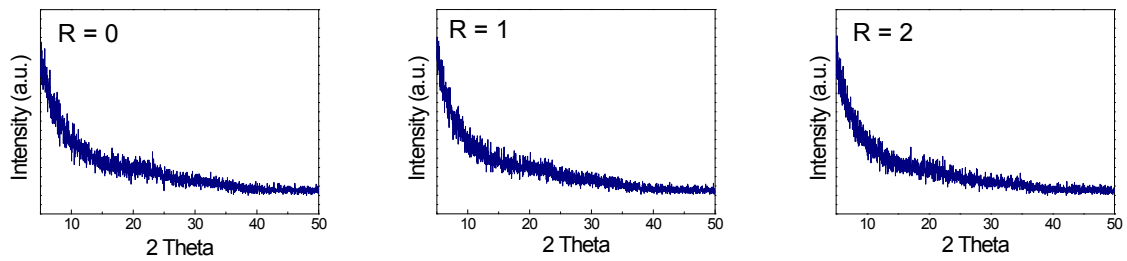


Figure S6. XRD results for ZTO channel layers from precursor solutions with R values of 0, 1, and 2. The molar ratio of Zn to Sn was 1.

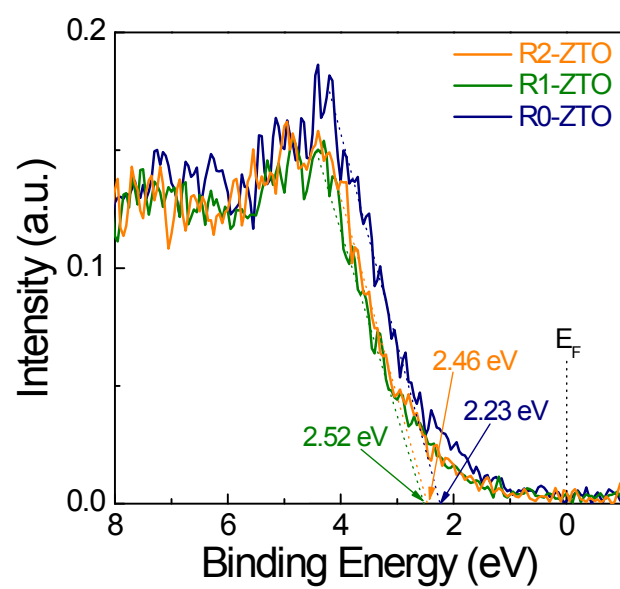


Figure S7. XPS spectra near the valence band for R0, R1, and R2-ZTO channel layers.