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Supporting Information

Alkali Earth Metal Dopants for high Performance and Aqueous-derived ZnO TFTs

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EXPERIMENTAL SECTION

Materials. Zinc oxide (99.999%, Aldrich), magnesium hydroxide monohydrate (99.95%, Aldrich), calcium hydroxide monohydrate (99.999%, Aldrich), Ammonia water (25.0~28.0 wt%; Daejung, Korea) were used without purification.

Preparation of alkali earth metal doped ZnO films. 0.001 mole of ZnO solution (ZnO powder 0.08139 g in 12 mL NH_4OH) was refrigerated for 5 hours to increase the solubility of ZnO. To enhance electrical properties of ZnO TFTs, 0.1 mL of $Mg(OH)_2$ and $Ca(OH)_2$ solution ($Mg(OH)_2$ powder 0.006 g in 10 mL de-ionized water and $Ca(OH)_2$ powder

0.0.0074 g, 0.0148 g in 10 ml de-ionized water) was added to the zinc oxide solution; this resulted in Mg and Ca doped ZnO solution. Because of different solubility in water (0.0014 g/100 mL of magnesium hydroxide and 0.173 g/100 mL of calcium hydroxide at 20 °C), magnesium dopant shows a low doping concentration (0.002 mol%). The prepared solution was spin-coated (3000 RPM, 30 s) on Si wafer with a thermally grown SiO_2 layer (thickness ~ 200 nm). The ZnO semiconductor films were annealed at 300 °C for 1hour.

Fabrication of TFTs. P-doped silicon wafer and a thermally grown SiO_2 layer (capacitance ~17 nF/cm^{-2}) were used as a gate electrode and a gate insulator, respectively. After annealing process, the TFTs were fabricated on alkali earth metal doped ZnO films. As source/drain electrodes, Aluminum (Al, 100 nm) was evaporated thermally on various ZnO thin films. Width/length ratio of electrode was 20 (1000 μm/50 μm). Field effect mobility was calculated from transfer curve through metal oxide semiconductor field effect transistor (MOSFET) standard model in the saturation regime, as follows.

$$I_D = \frac{W}{2L}\mu C_i (V_G - V_T)^2$$

I_D indicates the current between source and drain electrodes; W is the width of the channel; L is the length of channel; C_i is the capacitance of the dielectric layer; V_G is the voltage of gate electrode; and V_T is the saturation threshold voltage.

Observation of the ZnO thin films and TFTs. An atomic force microscope (AFM; XE100: PSIA) and a transmission electron microscope (TEM; JEM-2100F: JEOL) The current–voltage measurements were executed under ambient conditions by an Agilent 4155B semiconductor parameter analyzer. To exclude chemical reaction and interface diffusion of oxygen and moisture, bias stability tests were carried out in a vacuum condition (~5 mTorr).

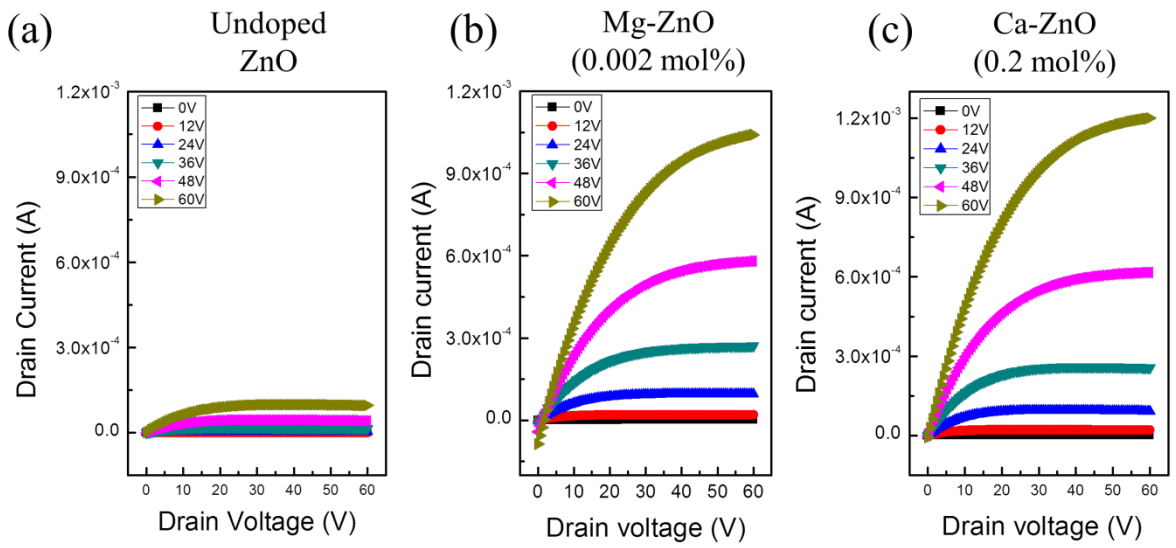


Figure S1. Output characteristic of various ZnO TFTs. (a) Undoped ZnO TFT, (b) Mg doped ZnO TFT (0.002 mol%), (c) Ca doped ZnO TFT (0.2 mol%).

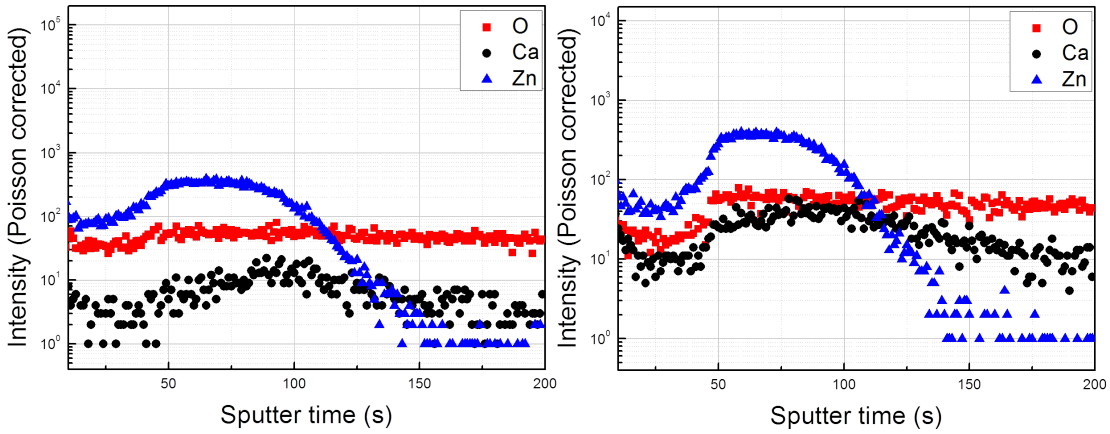


Figure S2. Time of flight – secondary ion mass spectroscopy (TOF-SIMS) data. (a) undoped ZnO film, (b) Ca doped ZnO film (0.2 mol%).

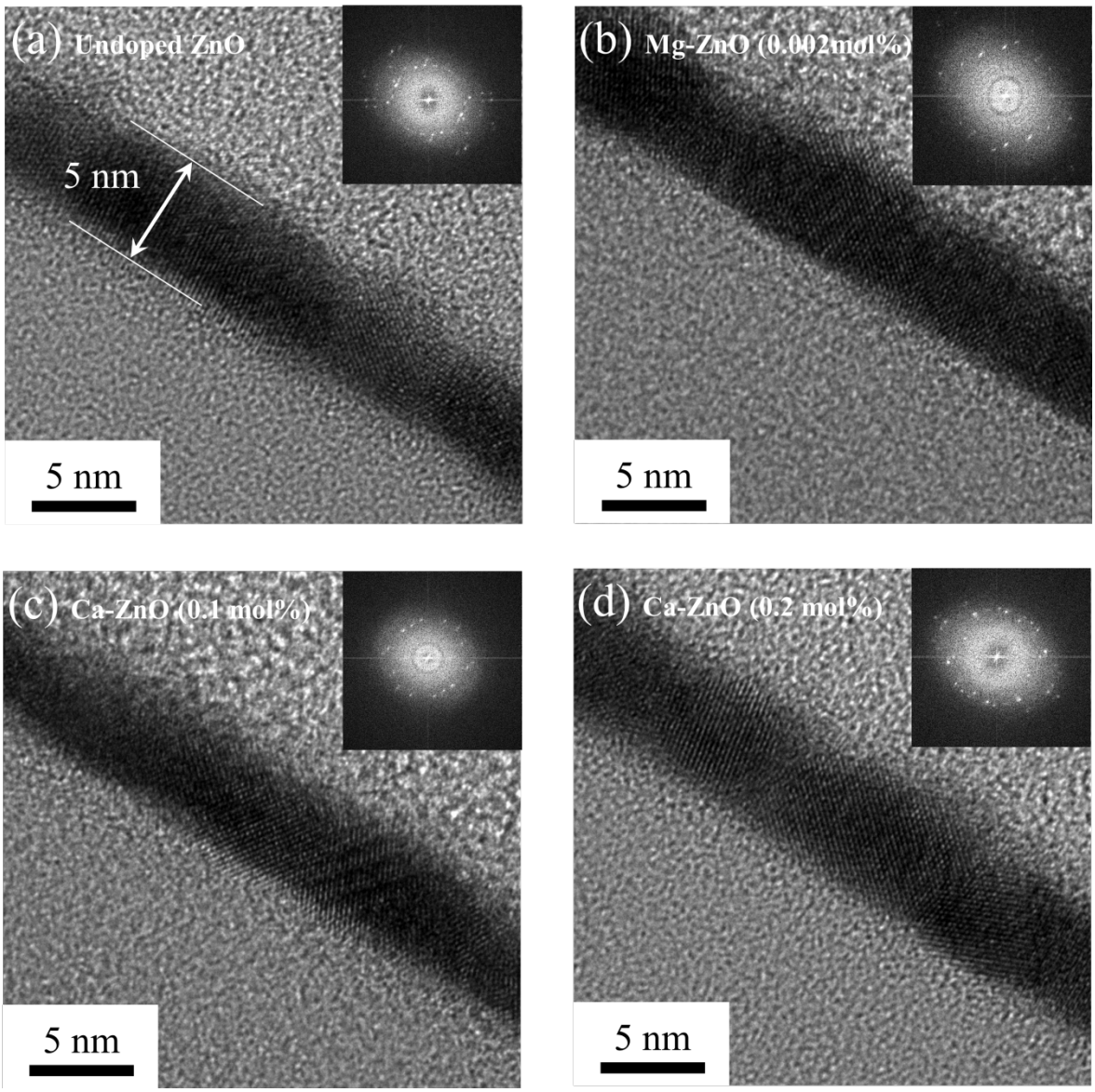
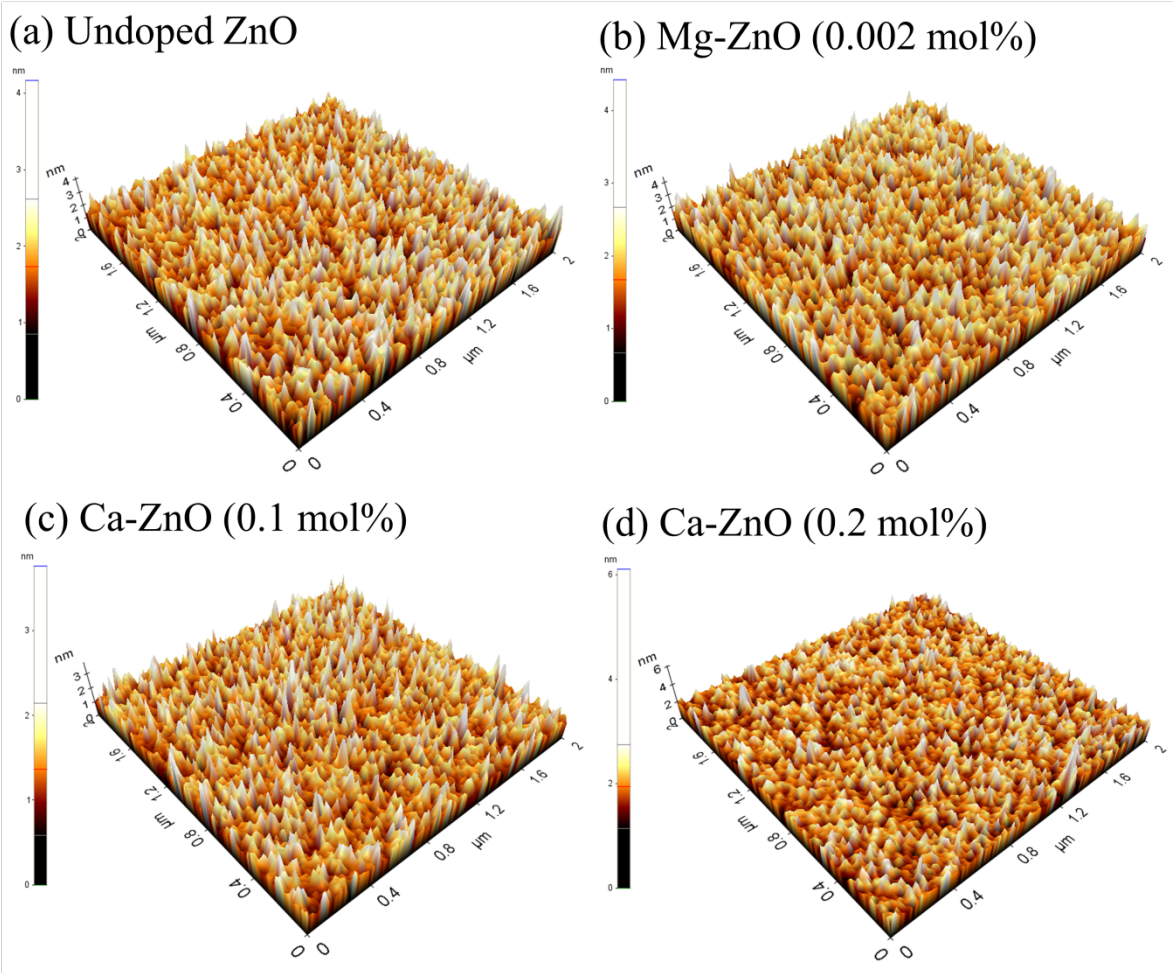


Figure S3. Cross-sectional HR-TEM images of alkali earth metal doped ZnO films on the SiO_2 substrate at annealing temperature 300 °C. (a) undoped ZnO film, (b) Mg doped ZnO film with 0.002 mol%, (c) Ca-doped ZnO film with 0.1 mol%, (d) Ca-doped ZnO film with 0.2 mol%. The inset image shows crystalline FFT-SAED patterns.



Figrue S4. Atomic force microscopy (AFM) images of alkali earth metal doped ZnO films. The root mean square (RMS) roughness values of ZnO films were 0.32 nm (undoped ZnO), 0.41 nm (Mg 0.002 mol%), 0.36 nm (Ca 0.1 mol%), and 0.408 nm (Ca 0.2 mol%).

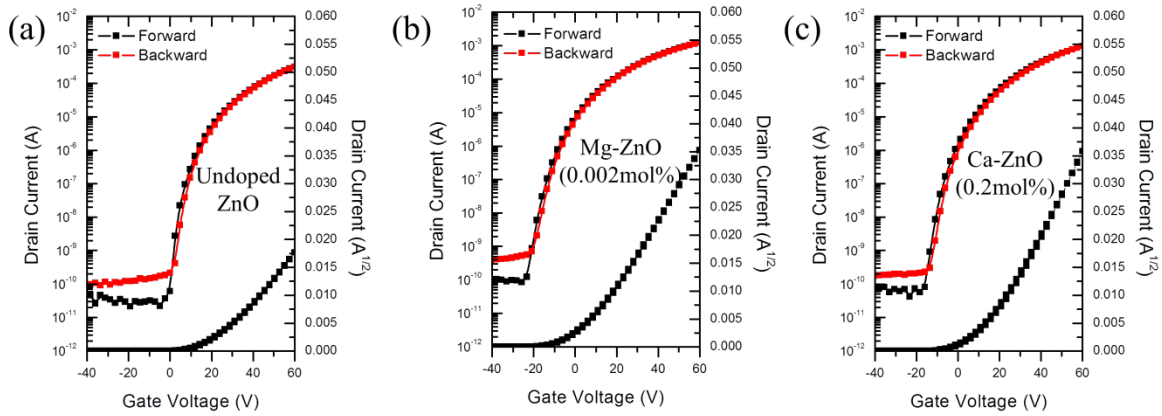


Figure S5. The hysteresis behavior of undoped and alkali earth metal doped ZnO TFTs with SiO_2 gate dielectric. (a) undoped ZnO, (b) Mg-ZnO (Mg 0.002 mol%), (c) Ca-ZnO (Ca 0.2 mol%).

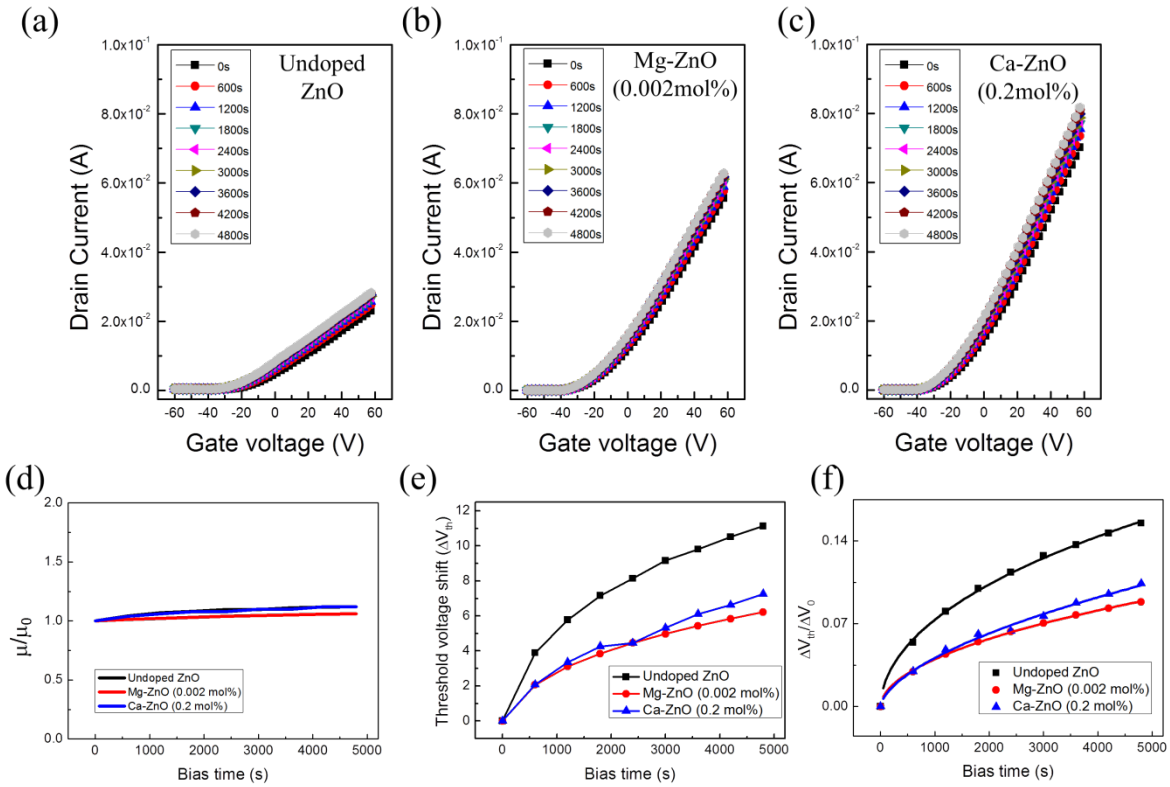


Figure S6. (a), (b) and (c) Evolution of the linear transfer curves of various ZnO TFTs, as a function of negative bias stress time (-40 V, 0-4800 s), (d) Relative field effect mobility of various ZnO TFTs, as a function of bias stress time (0-4800 s), (e) Relative threshold voltage shift (ΔVth) of various ZnO TFTs as a function of stress time, (f) Plot of ΔVth/Vo vs. bias stress time for un-doped, Mg (0.002 mol%) and Ca-doped ZnO (0.2 mol%) TFTs. The solid curves were fit to a stretched exponential equation.

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Sample	Concentration of elements in sample (ppm)
Ca-doped ZnO	651.86

Table S1. Concentration of elements in samples (ppm=mg/kg). ICP-AES data of Ca-doped ZnO powder shows the direct evidence of interstitial doping.

	Undoped ZnO	Mg-ZnO	Ca-ZnO
Mobility (cm^2/Vs)	1.34	4.86	6.02
V_{th} (V)	19	-10	-12
On/off current ratio	10^5	10^6	10^7
E_A (eV)	0.5017 (±0.0054)	0.54126 (±0.01756)	0.5140 (±0.00692)
K_BT (eV)	0.0298 (±0.0018)	0.03855 (±0.00516)	0.02819 (±0.00191)

Table S2. Electrical properties of various ZnO TFTs and E_A and K_BT_0 of undoped, Mg (0.002 mol%), and Ca-ZnO TFTs (0.2 mol%).