Electronic Supplementary Information

A novel regrowth method to simply prepare Li-doped ZnO nanorods and improve their photoluminescence properties

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Materials and Methods

Preparation of LZO films: The precursor solutions for the LZO films were prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, ACS Reagent, >98%, Sigma-Aldrich) and lithium chloride (LiCl, >99%, Sigma-Aldrich) in 2-methoxyethanol (99.8%, Sigma-Aldrich). The concentration of the metal precursors was 0.5 M. Monoethanolamine (C_2H_7NO, MEA, ACS Reagent, >99.0%, Sigma-Aldrich) was used as a stabilizing agent to improve the solubility of the precursor salt. The molar ratio of MEA to metal salts was 1.0 (1.204 mL), and the ratio of Li to Zn was fixed to 12 at.%. The mass of zinc acetate dihydrate and lithium chloride was 3.920 and 0.091 g, respectively. The volume of the precursor solution was 40 mL. The stabilized sol solution was stirred at 60 ºC for 2 h until it became clear and homogeneous. It was subsequently cooled to RT and aged for 24 h before it was used as the coating solution to deposit the films. The Si substrates were ultrasonically cleaned in acetone and ethanol for 10 min, rinsed with

deionized water, and blow-dried with nitrogen. The precursor solution was spin-coated onto a Si substrate at 2000 rpm for 20 s, and then the films were dried at 200 ºC for 10 min in an oven. These spin-coating and drying procedures were repeated five times.

Photoluminescence measurements: The photoluminescence (PL) properties of ZnO and Li-doped ZnO films were investigated via PL measurements using a He-Cd laser (325 nm) with an excitation power of 20 mW and a 0.75-m single-grating monochromator with a photomultiplier tube (HAMAMATSU, R928) using the photocount method.

Surface morphology characterization: The surface morphology was analyzed using a field-emission scanning electron microscope (HITACHI, S-4800).

Thermal analysis: The thermal analysis of the ZnO and LZO precursors was performed using a thermogravimetry-differential thermal analyzer (TA Instruments, SDT Q600) at a heating rate of 10 ºC/min in air.

Crystal orientation analysis: The crystal phase of the LZO films was investigated using an X-ray diffractometer (PANalytical X`Pert Pro, the Netherlands) with a Cu-Kα radiation source (λ = 0.154056 Å) and an accelerating voltage of 40 kV.

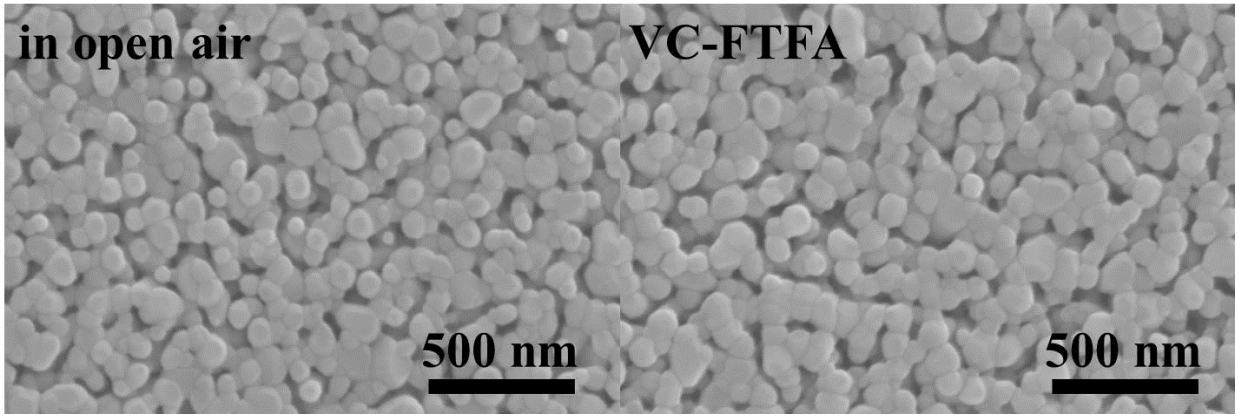

Fig. S1 SEM images of LZO films that were prepared using a lithium acetate precursor as the dopant and were annealed in open air and using the VC-FTFA method at 600 °C. The surface morphology did not change when LZO films were prepared using a lithium acetate precursor. As the temperature increased, the zinc acetate dihydrate gradually decomposed to form ZnO through the following chemical reactions:[1]

$$Zn(CH_3COO)_2 \cdot 2H_2O \rightarrow Zn(CH_3COO)_2 + 2H_2O(\uparrow) \quad (1)$$

$$4Zn(CH_3COO)_2 + 2H_2O \rightarrow Zn_4O(CH_3COO)_6 + 2CH_3COOH(\uparrow) \quad (2)$$

$$Zn_4O(CH3COO)_6 + 3H_2O \rightarrow 4ZnO + 6CH_3COOH(\uparrow) \quad (3)$$

$$Zn_4O(CH_3COO)_6 \rightarrow 4ZnO + 3CH_3COCH_3(\uparrow) + 3CO_2(\uparrow) \quad (4)$$

The chemical reactions of lithium acetate are similar to those of zinc acetate dihydrate. Therefore, according to chemical reactions (1–4), neither ZnO nor LZO was regrown when an acetate-based solvent was used because organic containing Zn and Li vapors were generated.

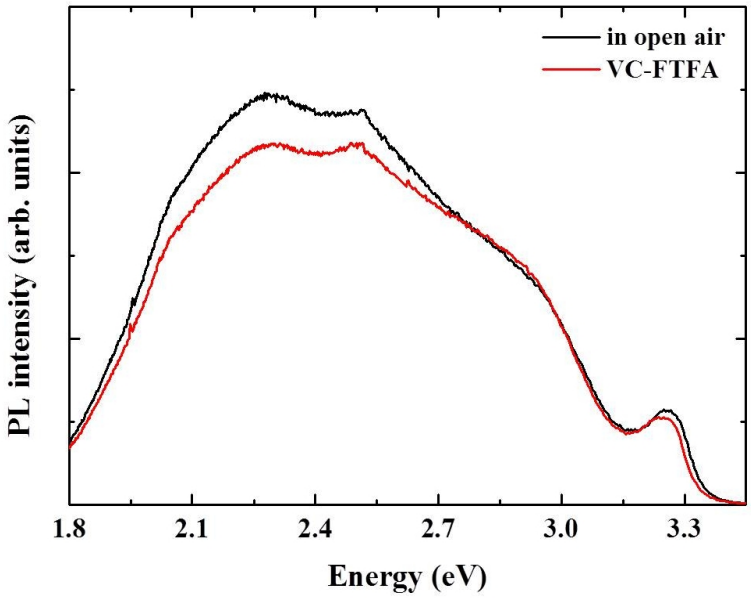

Fig. S2 PL spectra of LZO films that were obtained using a lithium acetate precursor as the dopant and were annealed in open air (black line) and using the VC-FTFA (red line) method at 600 °C.

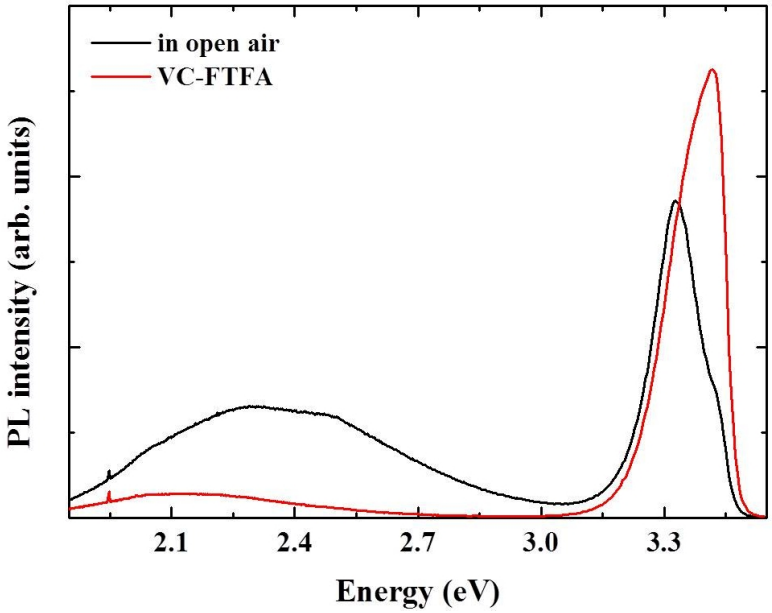

Fig. S3 PL spectra of Mg-doped ZnO films (20 at.%) annealed in open air (black line) and using the VC-FTFA (red line) method at 800 °C. The NBE emission peaks of the Mg-doped ZnO films annealed in open air and using the VC-FTFA method appear at 3.33 and 3.41 eV, respectively, indicating that VC-FTFA method using magnesium chloride precursor is excellent compositional control.

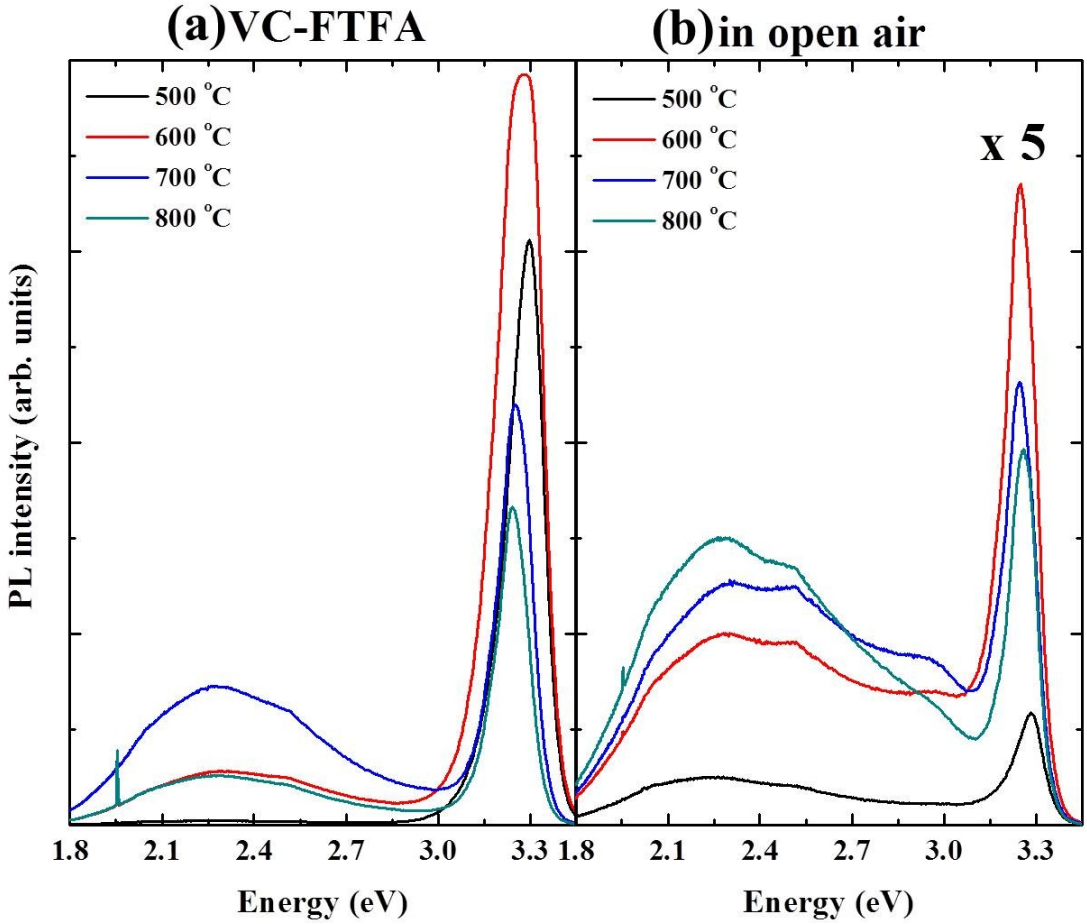

Fig. 4S PL spectra of LZO films annealed at various temperatures using the (a) VC-FTFA method and (b) in open air.

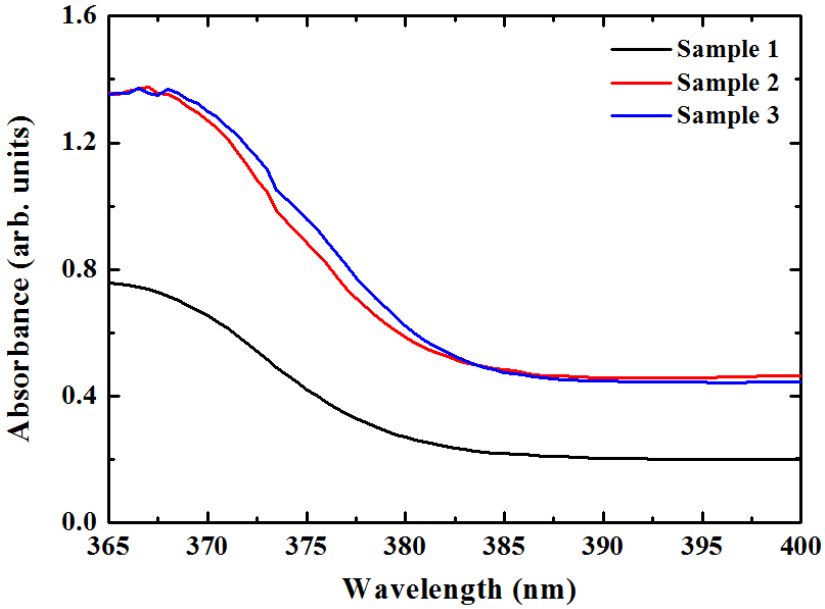

Fig. 5S Absorption spectra of three samples.

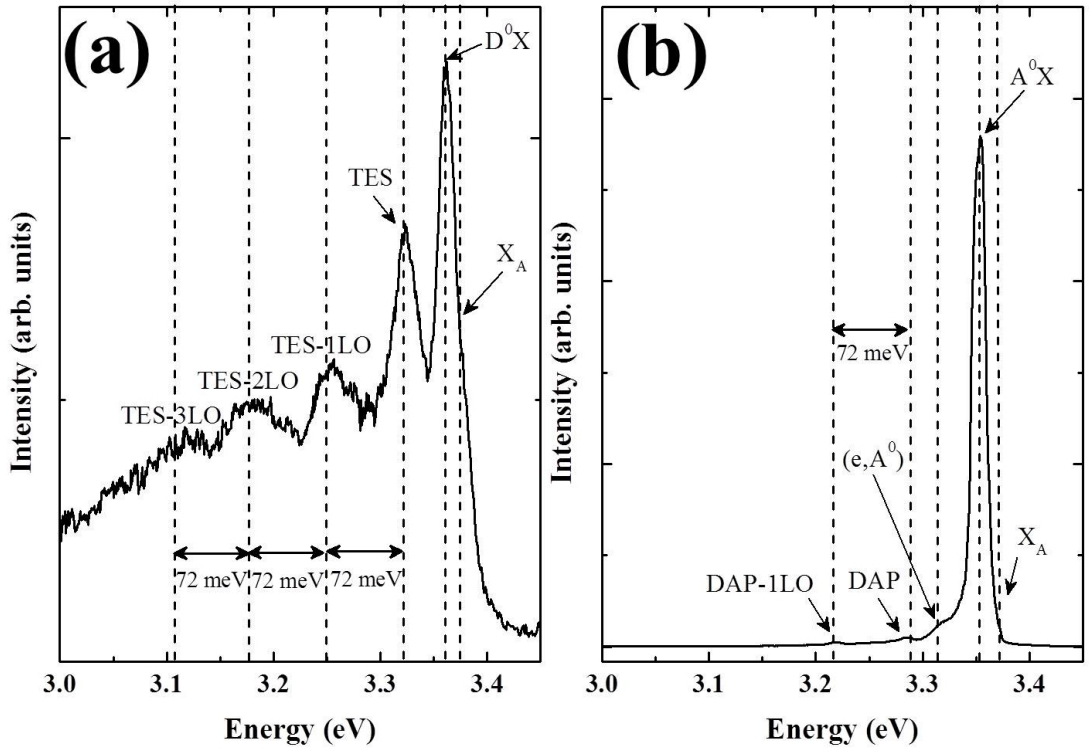

Fig. 6S PL spectra at 12 K of (a) a ZnO films that was annealed in open air and (b) sample 3, which was annealed using the VC-FTFA method.

References

1. C. -C. Lin and Y. -Y. Li, *Mater. Chem. Phys.* 2009, **113**, 334.