Supporting Information

Low-voltage and high-performance field-effect transistors based on $Zn_xSn_{1-x}O$ nanofibers with ZrO_x dielectric

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Experimental section

Precursor preparation. $Zn_xSn_{1-x}O$ precursor solutions were prepared by mixing zinc chloride ($ZnCl_2$) and tin chloride ($SnCl_2$) in N, N–dimethylformamide (DMF) with a total concentration of 0.2 M. The molar ratios of $ZnCl_2$ to $SnCl_2$ were set to be 0:1, 0.1:0.9, 0.3:0.7, 0.5:0.5, 0.7:0.3, 0.9:0.1 and 1:0 in precursor solutions, respectively. For convenience, the metal oxide nanofibers fabricated by using the precursor solutions with various molar ratios are termed to be SnO_2, $Zn_{0.1}Sn_{0.9}O$, $Zn_{0.3}Sn_{0.7}O$, $Zn_{0.5}Sn_{0.5}O$, $Zn_{0.7}Sn_{0.3}O$, $Zn_{0.9}Sn_{0.1}O$, and ZnO, respectively. In a typical procedure for electrospinning, poly vinyl pyrrolidone (PVP, MW=1,300,000) was added to $Zn_xSn_{1-x}O$ solutions to produce the final $Zn_xSn_{1-x}O$ precursor solutions. The final $Zn_xSn_{1-x}O$ precursor solutions were stirred at room temperature for 6 h, and sticky and clear solutions were obtained subsequently. The stock solutions were stable and no precipitation was observed during weeks of usage. The precursor solution for ZrO_x was prepared by dissolving zirconium nitrate pentahydrate [$Zr(NO_3)_4{\cdot}5H_2O$] in 2-methoxyethanol with a concentration of 0.15 M. The precursor solution was stirred at room temperature for 12 h to form homogenous and transparent solution.

Nanofibers fabrication and device integration. Heavily doped p-type Si wafers with resistivity of 0.001 Ω cm were used as the gate electrodes and substrates. The Si substrates were cleaned ultrasonically in 2% HF acid, acetone, ethanol, and de-ionized water in sequence and dried by N_2 gun. The substrates were exposed under oxygen plasma for 5 min to enhance the hydrophilicity. ZrO_x solution was filtered through 0.22 μm polytetrafluoroethylene (PTFE) syringe filter and then spun on the hydrophilic Si substrates at a speed of 500

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rpm for 5 s and 5500 rpm for 20 s. The obtained films were baked at 150 °C for 20 min. In order to photolyze and densify the gel films, the samples were cured under a high-pressure mercury UV lamp for 40 min and annealed at 550 °C for 2 h in air.[1]

$Zn_xSn_{1-x}O$ precursor solutions were then delivered into a metallic needle with an inner diameter of 0.34 mm with a constant flow rate of 0.5 mL/h by a peristaltic pump. High voltage of 15 kV was supplied at the metallic needle by a DC power supply. A piece of aluminium foil was grounded and placed 15 cm away from the tip of the needle to collect the nanofiber networks (NFNs). The collecting time was set to be 27 s. The solution jet was solidified with accompanying evaporation of solvent and continuous nanofibers were formed on the collector. To obtain the FETs based on $Zn_xSn_{1-x}O$ NFNs, heavily doped p-type Si substrates with thermally-grown 100 nm SiO_2 layer (or ZrO_x dielectric thin film) was attached to the aluminium foil. The as-electrospun NFNs were collected on the substrate and then treated by UV lamp for 40 min.[2] Subsequently, the NFNs were calcined at 500 °C for 2 h in air. Finally, the aluminium source and drain electrodes were deposited by thermal evaporation through a shadow mask. The channel width and length were 1000 and 100 μm, respectively.

Nanofibers and devices characterization. Thermogravimetric analysis (TG-DSC, NETZSCH, STA 449 F3) was used to investigate the thermal behaviour of the dried $Zn_xSn_{1-x}O$ precursor solution. The crystal structures of $Zn_xSn_{1-x}O$ nanofibers were investigated by X-ray diffractometer (XRD, X'Pert-PRO MPD and MRD, PANalytical, Holland) with a Cu Kα1 radiation. The electrical performance of the FETs was measured by using a semiconductor parameter analyzer (Keithley 2634B) under ambient conditions in a dark box. The surface morphologies of $Zn_xSn_{1-x}O$ nanofibers were characterized by using field-emission scanning electron microscope (FESEM, Zeiss MERLIN Compact) and high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100F). Energy dispersive spectrometer (EDS, attached to the HRTEM) was used to analyze the elemental distribution of the obtained $Zn_xSn_{1-x}O$ nanofibers. The μ_{FE} was calculated using the following equation[3]

$$I_{DS} = \frac{W}{2L}\mu_{FE}C_i(V_{GS} - V_{TH})^2$$

where C_i is the areal capacitance of the gate dielectric; L and W are the channel length and width of the FETs, respectively; V_{GS} is the gate voltage and V_{TH} is the threshold voltage, which is estimated from linear fits to the dependence of $I_D^{1/2}$ on V_{GS}. The subthreshold swings (SS) was calculated using the following equation [4]

$$SS = \left[\frac{d\log(I_{DS})}{dV_{GS}}\right]^{-1}$$

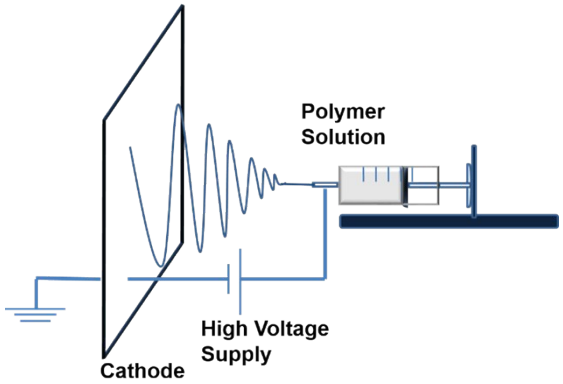

Fig. S1 Schematic of electrospinning process.

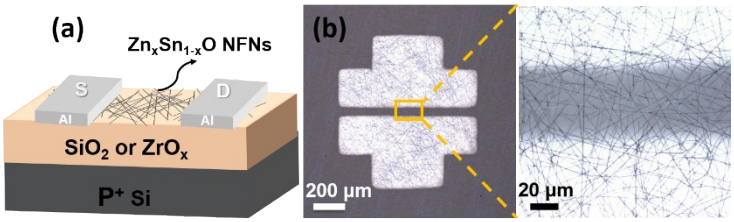

Fig. S2 (a) Schematic diagram of FETs used in this study. (b) Typical optical microscopy image of the FETs based on $Zn_{0.3}Sn_{0.7}O$ NFNs and inset of the relative channel amplification diagram of the selected area marked with an orange rectangle in (b).

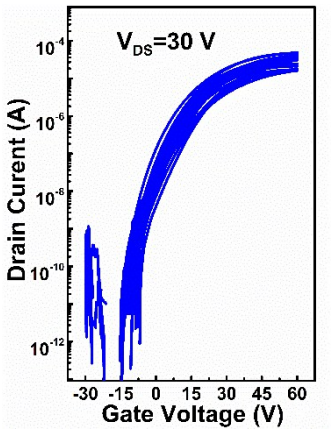

Fig. S3 Transfer curves of the electrospun $Zn_{0.3}Sn_{0.7}O$ NFNs/SiO_2 FETs (3×5 array) at V_{DS} = 30 V.

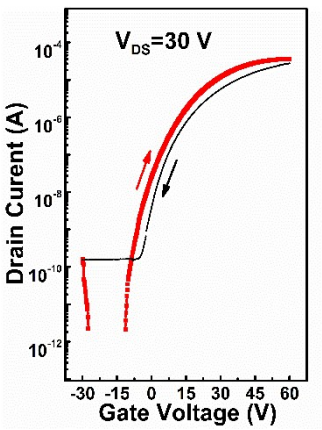

Fig. S4 Transfer curves of the electrospun $Zn_{0.3}Sn_{0.7}O$ NFNs/SiO_2 FETs measured with forward and reverse sweep.

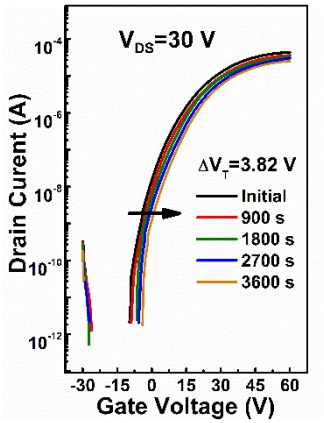

Fig. S5 Transfer curves of $Zn_{0.3}Sn_{0.7}O$ NFNs/SiO_2 FETs under PBS tests for 3600 s.

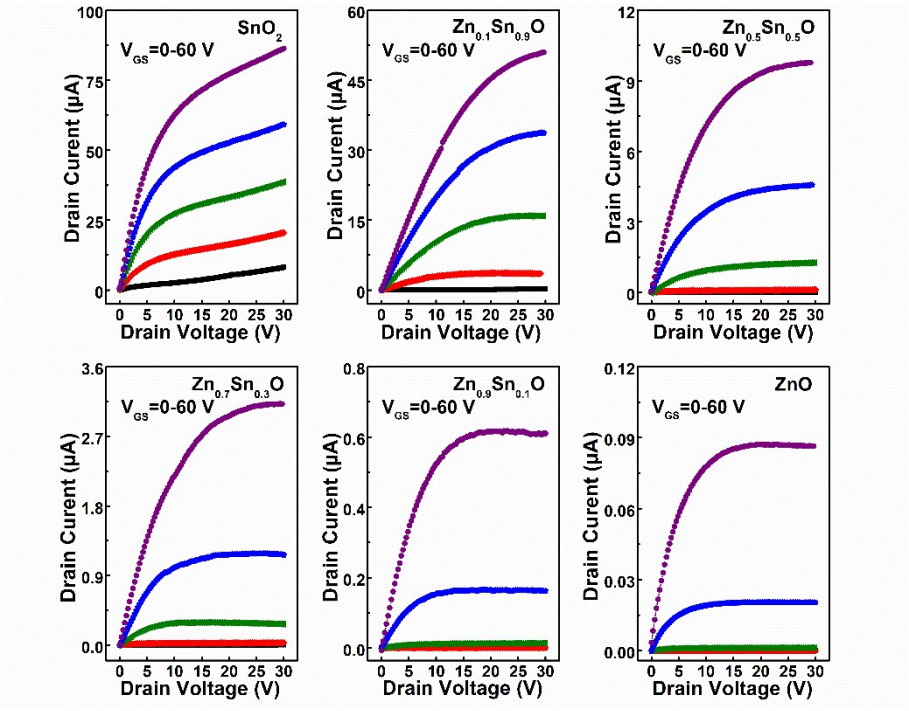

Fig. S6 Output characteristics of the FETs based on $Zn_xSn_{1-x}O$ NFNs with various Zn to Sn molar ratios on SiO_2 dielectric.

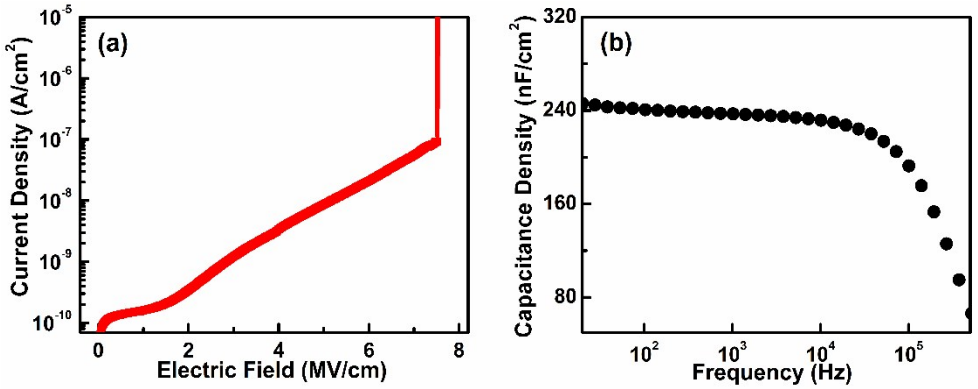

Fig. S7 (a) leakage current density and (b) areal capacitance of ZrO_x dielectric.

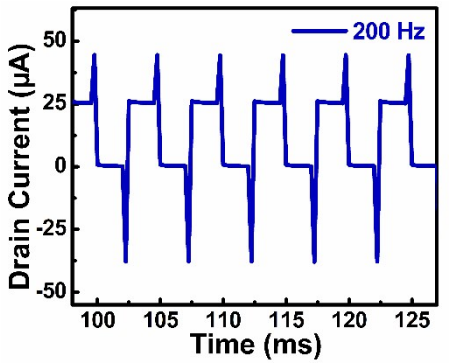

Fig. S8 Drain current responses to a square wave signal applied to the gate voltage with 200 Hz frequency.

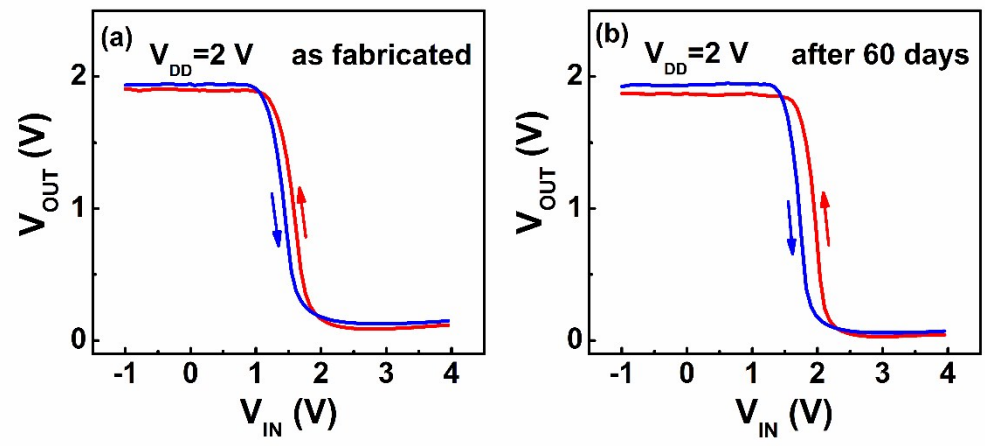

Fig. S9 VTC curves of inverter based on $Zn_{0.3}Sn_{0.7}O$ NFNs/ZrO_x FETs, with forward and reverse sweep, measured immediately after fabrication (a) and measured 60 days later (b).

Table S1. Key electrical parameters of the FETs based on $Zn_xSn_{1-x}O$ NFNs/SiO_2 with various Zn to Sn molar ratios.

Zn : Sn molar ratio	μ_{FE} ($cm^2\ V^{-1}\ s^{-1}$)	V_{TH} (V)	$I_{on/off}$	SS ($V\ dec^{-1}$)
0:1	0.20 ± 0.03	-14.56 ± 5	~ 10^3	3.19 ± 0.2
0.1:0.9	0.18 ± 0.023	-4.35 ± 4	~ 10^5	3.42 ± 0.5
0.3:0.7	0.17 ± 0.02	6.25 ± 4	~ 10^7	3.56 ± 0.3
0.5:0.5	0.05 ± 0.016	9.37 ± 3	~ 10^7	3.66 ± 0.2
0.7:0.3	0.02 ± 0.011	15.63 ± 4	~ 10^6	3.80 ± 0.4
0.9:0.1	10^{-3}-10^{-2}	18.27 ± 6	~ 10^6	4.10 ± 0.5
1:0	~ 10^{-3}	24.52 ± 5	~ 10^5	5.04 ± 0.2

References

1. G. Liu, A. Liu, F. Shan, Y. Meng, B. Shin, E. Fortunato and R. Martins, *Appl. Phys. Lett.*, 2014, **105**, 113509.
2. A. Liu, Y. Meng, H. Zhu, Y. Y. Noh, G. Liu and F. Shan, *ACS Appl. Mater. Interfaces*, 2017, doi: 10.1021/acsami.7b08794.
3. T. Jun, Y. Jung, K. Song and J. Moon, *ACS Appl. Mater. Interfaces*, 2011, **3**, 774-781.
4. C. Wang, Y. Meng, Z. Guo, B. Shin, G. Liu and F. Shan, *Appl. Phys. Lett.*, 2018, **112**, 213501.