Electronic Supplementary Information (ESI)

Sublimation-Doping with Super Bases for High-Performance Solution-Processed Heterojunction Oxide Thin Film Transistors

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Experimental Section

Base preparation

In amidine-based organic dopants, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Sigma-Aldrich. For synthesis of 1,1-(1,10-Decanediyl)bis[1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-α]pyrimidine] (2TBD-C10), 1,10-dibromodecane and NaH (60%, dispersion in paraffin liquid) were purchased from TCI. $CDCl_3$ and anhydrous THF were purchased from Sigma Aldrich. n-Hexane and dichloromethane (DCM) were purchased from Daejung Chemicals Korea. To the oven-dried 50 ml Schlenk flask with stir bar under nitrogen, dry THF (50 mL) was loaded followed by the addition of NaH (60%, dispersion in paraffin liquid, 0.39 g, 9.33 mmol). After 0.5 h, TBD (1 g, 7.18 mmol) was slowly added and stirring was further continued for 4 h followed by addition of 1,10-dibromodecane (0.91 g, 2.87 mmol). Reaction mixture was stirred at room temperature overnight under nitrogen. The crude mixture was filtered and rinsed with DCM. The filtrate was evaporated under reduced pressure to yield a white waxy solid which was purified by dissolving in small amounts of hexane (5 mL). The hexane fractions were collected and evaporated under reduced pressure. This was repeated for 3 times such that colorless liquid was remained without any impurities. 2TBD-C10 was obtained as white waxy solid (0.954 g, 79 % yield).[S1]

Precursor preparation

For spin coating of In_2O_3, indium nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$) was dissolved in deionized water (DIW) to achieve a 0.1 M and stirred at room temperature for 6 h before use. For spin coating of ZnO, 1.0 g of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was dissolved in 10 mL of 2-methoxyethanol and 0.28 mL of ethanolamine. The ZnO precursor solution was stirred at 60°C for 3 h before use. For ZrO_2 dielectric layer, zirconium(Ⅳ) acetylacetonate ($Zr(C_5H_7O_2)_4$) was dissolved in 5 mL of dimethylformamide (DMF) and 30.18 µL of ethanolamine to achieve a 0.1 M and stirred at 70°C for 3 h before use. All materials required for the experiments were used as received from Sigma-Aldrich without any pretreatment.

Thin film fabrication

Highly doped silicon (Si^{++}) as the gate electrode and 300 nm thick thermally grown SiO_2 as gate dielectric layer were used as the substrate of TFT. To remove organic residues from substrates, these were cleaned by piranha solution that is a mixture of sulfuric acid (H_2SO_4) : 30% of hydrogen peroxide (H_2O_2) (7:3), followed by O_2 plasma for 5 min. For ZrO_2 dielectric layers, the ZrO_2 precursor solution was filtered by 0.2 µm PTFE filter and the Si wafers were spin-coated at 4000 rpm for 30 s and treated by UV irradiation for 40 min. Then, the substrates were annealed at 300°C for 1 h. The areal capacitance of ZrO_2 layer was measured as 370 $nFcm^{-2}$ by 4284A Precision LCR Meter. For the heterojunction active layer, the In_2O_3 precursor solution was first spin coated at 3000 rpm for 30 s and subsequently annealed at 260°C for 1 h. After cooling for enough time, the ZnO precursor solution was spin coated at 4000 rpm for 30 s. For sublimation-based doping, the films were exposed to vapor of the amidine-based organic dopants such as DBU, TBD, and 2TBD for different time (3, 6, and 9 min) in glove box. In DBU doping, the vapor was generated by heating one drops of DBU solution in a covered glass bottle at 80°C on a hot plate.[S2] In TBD and 2TBD doping, the vapor was generated by heating 0.1 mmol of TBD and 2TBD powder in a covered glass bottle at 150°C and 210°C, respectably, on a hot plate. After sublimation-doping, the substrates were annealed at 210°C for 1 h. TFTs were completed with the 100 nm thick thermal deposition of Al source and drain electrodes under high vacuum condition through metal shadow masks.

Device characterization

The electrical characterizations of the transistors such as transfer, output, C-V, breakdown voltage, and bias-stress stability characteristics were performed at room temperature in a nitrogen glove box using a Keithley 2450 parameter analyzer. The electron mobility was evaluated in the saturation region by[S3]

$$\mu_{sat} = \frac{L}{WC_1}\frac{\partial^2 I_{D,sat}}{\partial V_G^2}$$

where L and W are the length and width of the channel, respectably, C_1 is the capacitance of the gate dielectric, $I_{D,sat}$ is the saturation drain current, and V_G is the gate voltage.

UPS and XPS were performed with an ESCALAB 250Xi photoelectron spectrometer under high vacuum and an ultraviolet source of He I (21.2 eV) was used. Depth profile analysis was performed by SIMS (IMS 6F, CAMECA) using impact energy of 5 keV and current of 5 nA.

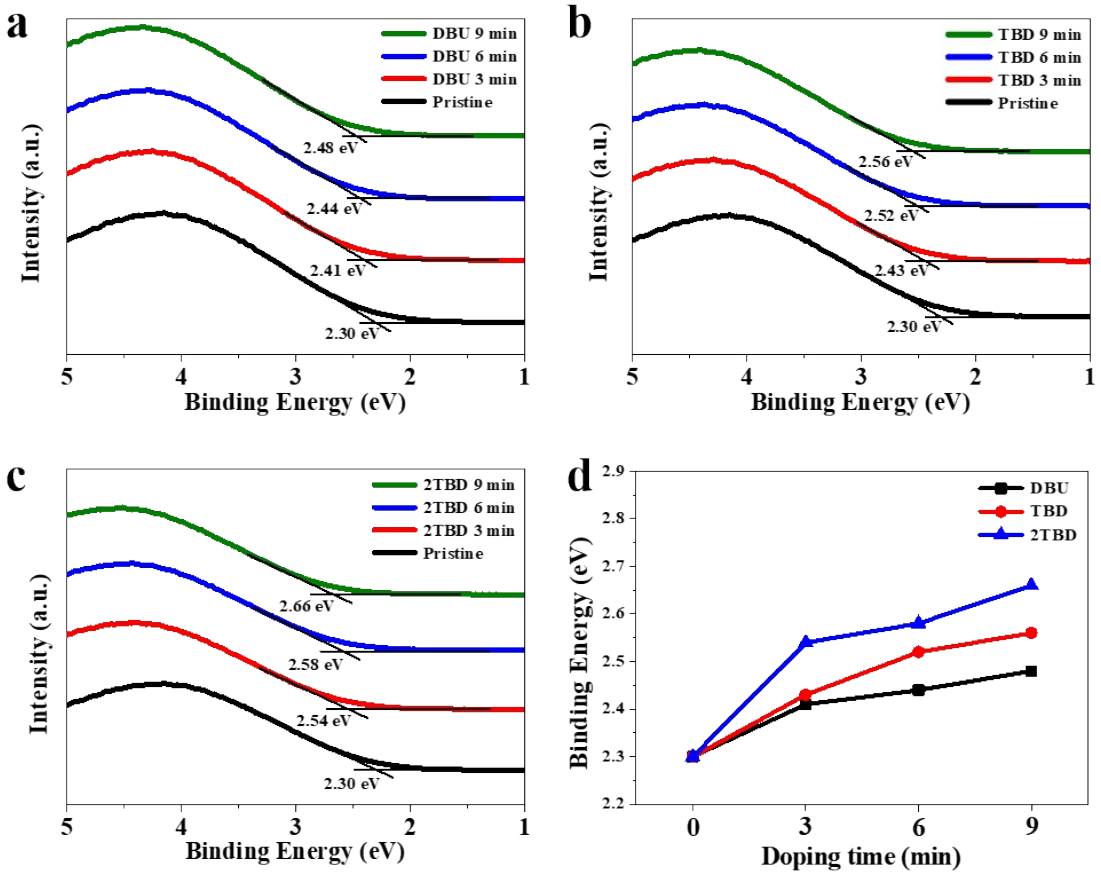

Fig. S1 UPS spectra of ZnO layer with different sublimation-doping times of DBU, TBD, and 2TBD. The valence band edge of UPS spectra shows distance between the Fermi energy level and valence band by doping ZnO layer with a) DBU, b) TBD and c) 2TBD. d) Changes of the valence band edge as a function of doping times and types of dopants.

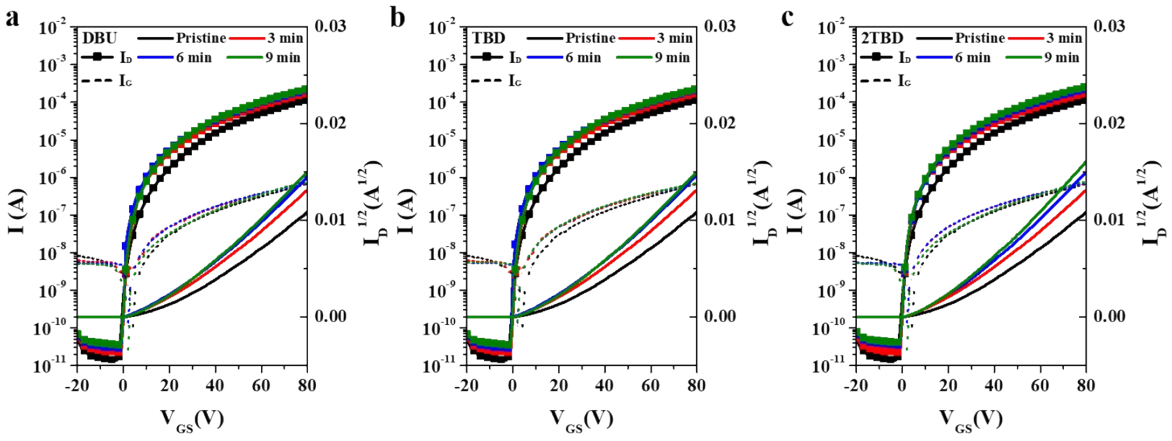

Fig. S2 Representative transfer characteristics of ZnO TFT with SiO_2 gate dielectric a) DBU- b) TBD-, c) 2TBD-doping with various times of sublimation-doping, measured at V_D = 80 V.

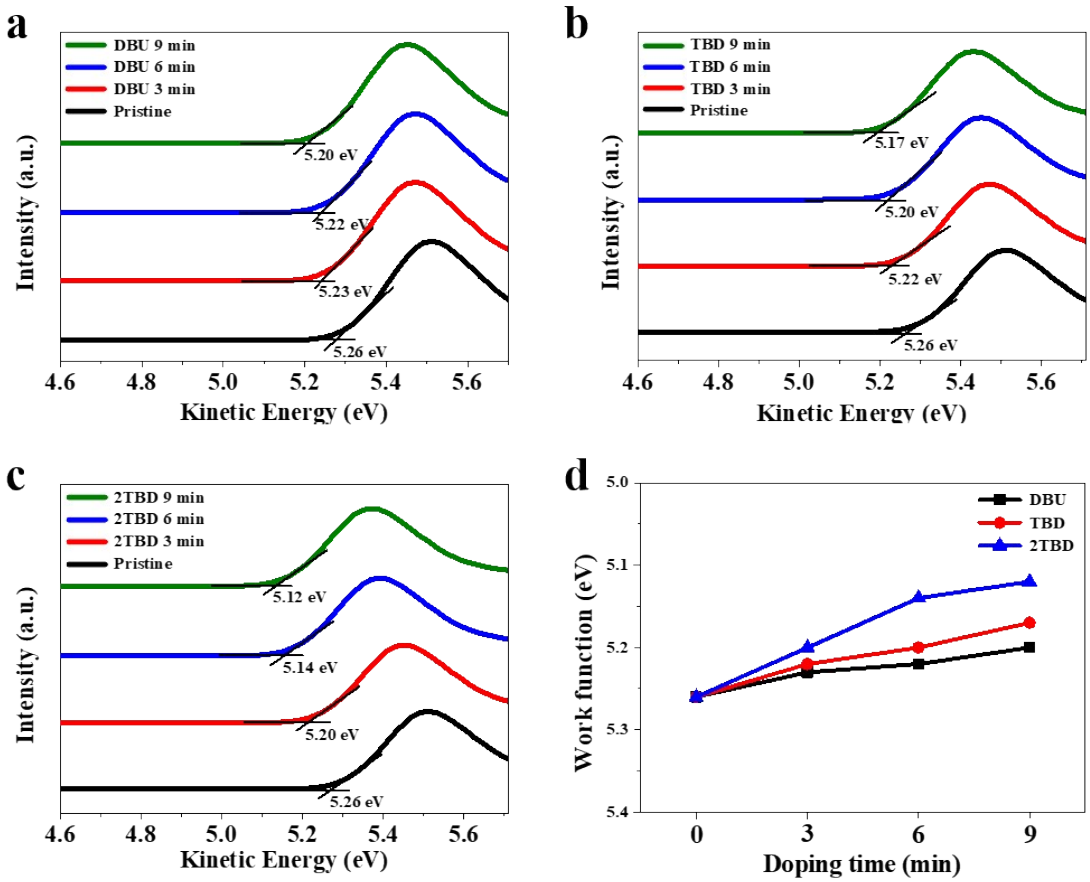

Fig. S3 UPS spectra of In_2O_3 layer with different sublimation-doping times of DBU, TBD, and 2TBD. The secondary cut-off edges of UPS spectra show work function changes by doping In_2O_3 layer with a) DBU, b) TBD and c) 2TBD. d) Change of work functions as a function of doping times and types of dopants.

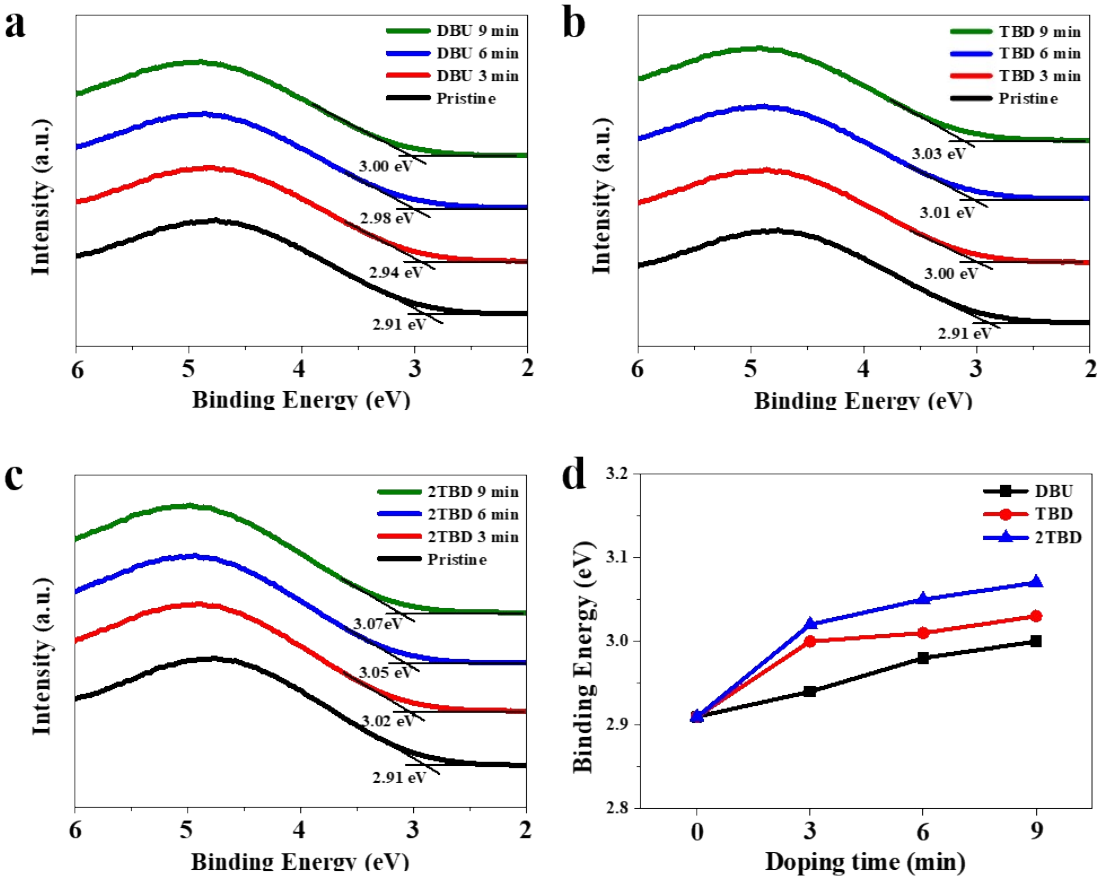

Fig. S4 UPS spectra for In_2O_3 layer with different sublimation-doping times of DBU, TBD, and 2TBD. The valence band edge of UPS spectra shows distance between the Fermi energy level and valence band by doping In_2O_3 layer with a) DBU, b) TBD and c) 2TBD. d) Changes of the valence band edge as a function of doping times and types of dopants.

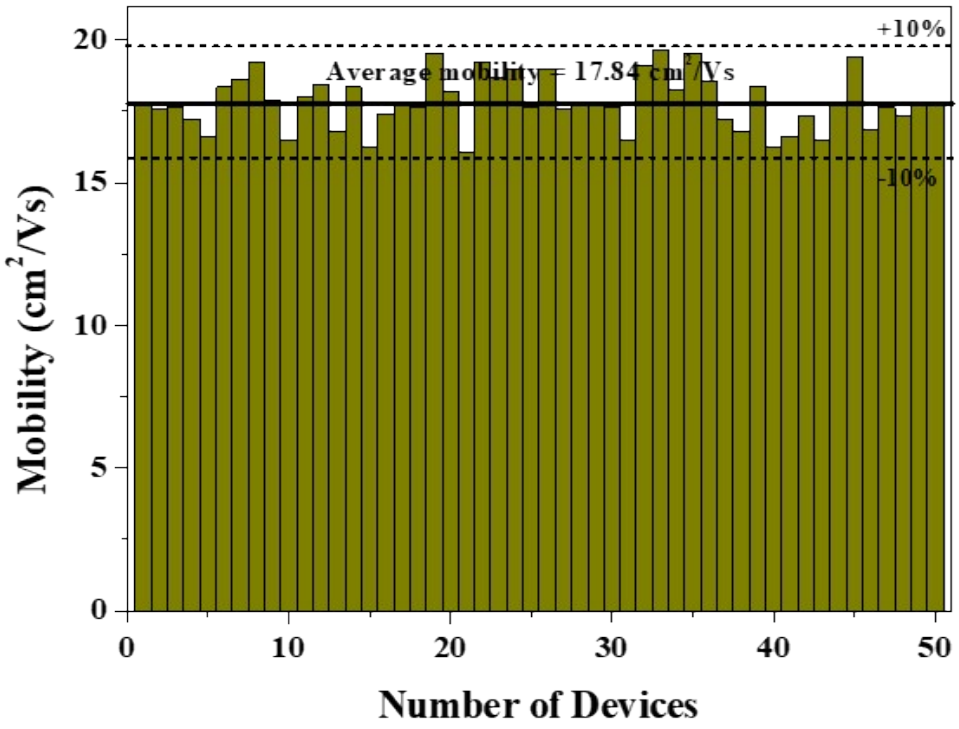

Fig. S5 Histograms of the mobility for 6 min 2TBD doped In_2O_3/ZnO heterojunction TFT with SiO_2 gate dielectric. Reproducibility tests are conducted for 50 independently fabricated TFTs using the optimized condition, and electron mobility distributions with deviation <±10% are demonstrated.

Table S1 Trap density of ZnO and In_2O_3/ZnO TFTs for Si/SiO_2 (300 nm) substrates.

ZnO	Pristine	DBU 3min	DBU 6min	DBU 9min	TBD 3min	TBD 6min	TBD 9min	2TBD 3min	2TBD 6min	2TBD 9min
V_{Th} (V)	8.81	9.12	10.15	11.13	9.79	10.77	10.46	9.48	10.46	11.80
N_{tr} ($x10^{11}cm^{-2}$)	6.06	6.27	6.97	7.65	6.74	7.40	7.19	6.52	7.19	8.11
In_2O_3/ZnO	Pristine	DBU 3min	DBU 6min	DBU 9min	TBD 3min	TBD 6min	TBD 9min	2TBD 3min	2TBD 6min	2TBD 9min
V_{Th} (V)	6.11	6.12	8.31	9.22	6.33	7.05	7.77	5.96	7.05	6.69
N_{tr} ($x10^{11}cm^{-2}$)	4.21	4.20	5.71	6.33	4.35	4.84	5.34	4.10	4.84	4.59

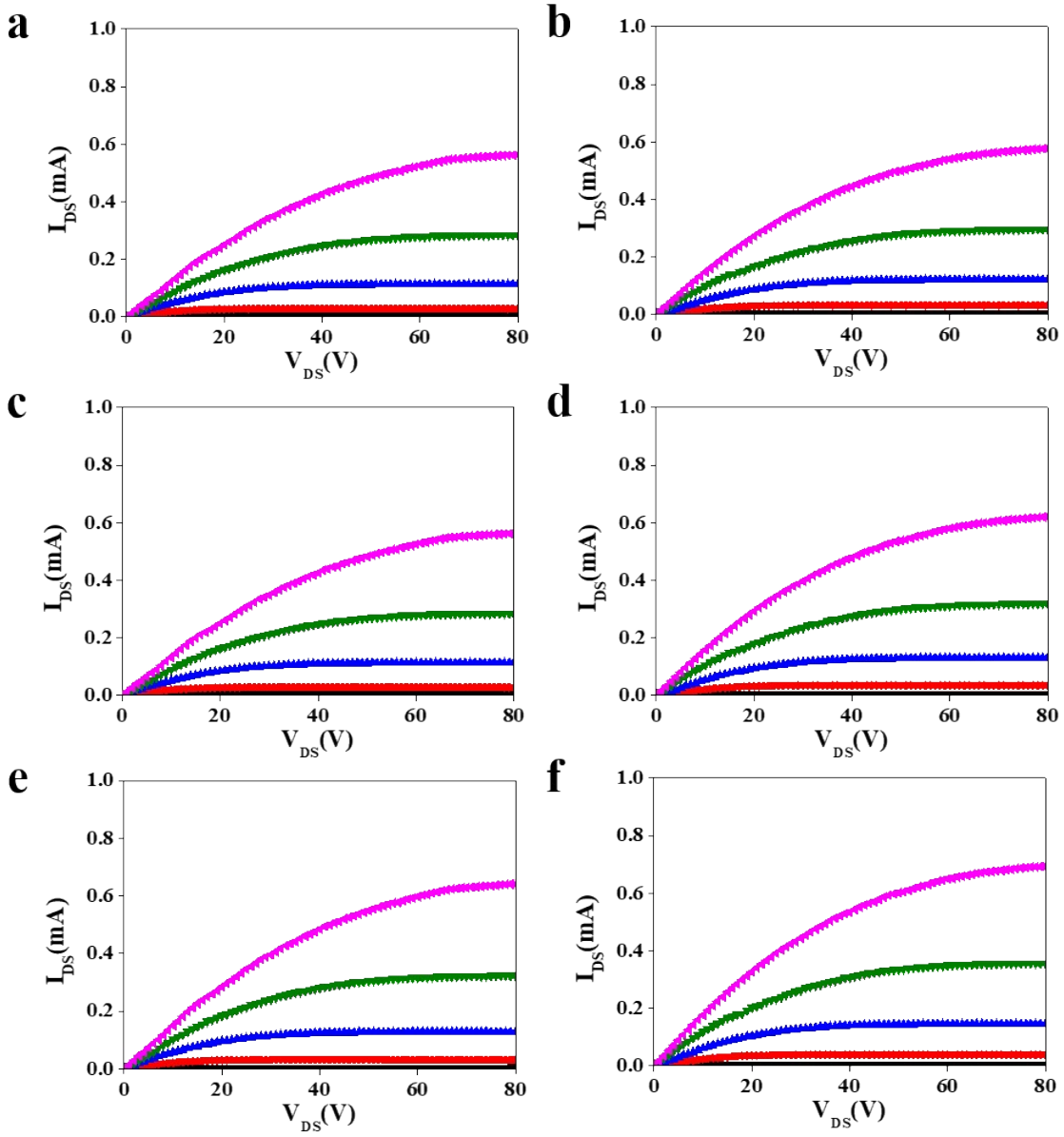

Fig. S6 Output characteristics of In_2O_3/ZnO heterojunction TFT with a) 3 min DBU-, b) 9 min DBU-, c) 3 min TBD-, d) 9 min TBD-, e) 3 min 2TBD-, f) 9 min 2TBD-doping with SiO_2 gate dielectric. The gate voltage was increasingly varied between 0 V and 80 V in step of 20 V.

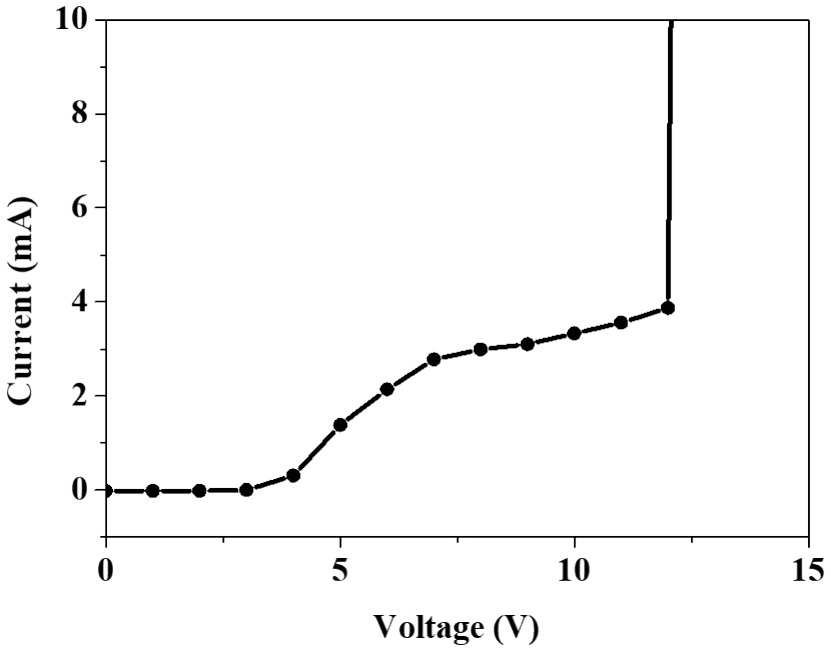

Fig. S7 Breakdown voltage characteristics of dielectric layer in a MIM capacitor.

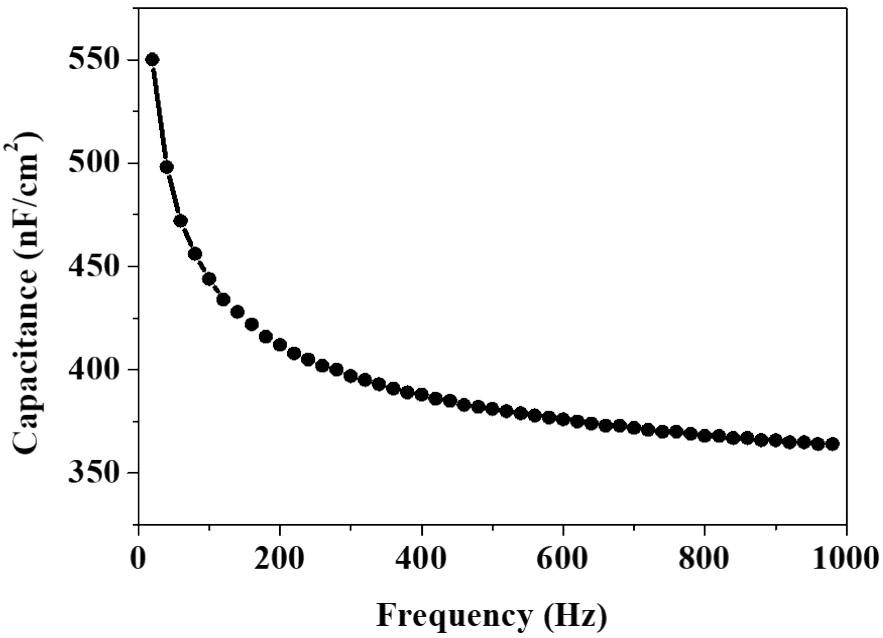

Fig. S8 Capacitance-frequency characteristics of dielectric layer in a MIM capacitor.

Reference

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S2. L. Hu, T. Liu, J. Duan, X. Ma, C. Ge, Y. Jiang, F. Qin, S. Xiong, F. Jiang, B. Hu, X. Gao, Y. Yi, Y. Zhou, Adv. Funct. Mater., 2017, **27**, 1703254.

S3. D. Nirmal, J. Ajayan, Handbook for III-V High Electron Mobility Transistor Technologies, CRC Press, Boca Raton 2019.