Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Control of Resistive Switching Voltage and Reduction of High-Resistive-State Current of Zinc Oxide by Self-Assembled Monolayers

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Contents

1. Experimental

1. Materials

We used zinc acetylacetonate hydrate ($Zn(AcAc)_2$, 99.995%, trace metals basis, Sigma-Aldrich) as a precursor for electron transporting layer film. The indium tin oxide (ITO) substrates (sheet resistance = 10 Ω sq) and Al (99.99%) were purchased from Furuuchi Chemical Corporation. Triethylsilane compounds and organic solvents for SAM-treatment were purchased from Tokyo Chemical Industry Co. Ltd. (TCI).

2. Fabrication of ZnO-based resistive memories

An ITO-coated glass substrate was cleaned by ultrasonication in isopropanol. The ZnO precursor solution was prepared by dissolving $Zn(AcAc)_2$ (95 mg) in 2-methoxyethanol (10.0 mL) with small amount of acetyl acetone. A ZnO layer was prepared by spin coating of the precursor solution (1000 rpm, 60 s) and subsequent thermal annealing for 60 min at 250°C under ambient conditions. After preparation of SAMs on the ZnO, an Al electrode was deposited by thermal evaporation under vacuum through a metal mask (active area: 10 mm^2). The current-voltage measurements were performed under nitrogen conditions using Keithley 4200A-SCS PARAMETER ANALYZER.

3. Preparation of SAMs on the ZnO films

After the UV/ozone treatment of the ZnO-prepared ITO, SAM was formed on the activated substrates by immersing in a toluene solution of triethoxysilane compounds (50 mM) for 15 min at 60°C. Then, the substrate was rinsed with pure toluene and acetone. Following the final rinse step, the substrate was annealed on a hot plate at 120°C for 5 minutes under N_2 atmosphere, and then the substrate was thoroughly washed with boiling toluene.

3. Analytical measurements

ATR-IR spectra were recorded on FT/IR-460plus (JASCO Corporation). AFM images were measured with a SII SPI3800N AFM apparatus. WF values were measured by using Trek model 320C electrostatic voltmeter with Kelvin probe unit. XPS analysis were performed by using Shimadzu AXIS-ULTRA DLDXPS apparatus. AC-impedance measurements were carried out using E4980A precision LCR meter (Agilent) under simulated sunlight irradiation. The frequency range was from 20 Hz to 1 MHz, the alternating signal magnitude was 5 mV and DC bias was 0 V. The data obtained were fitted with Scribner Associates Z-VIEW software v3.1 using the appropriate equivalent circuits. Water contact angles were observed using DMs-200 (Kyowa Interface Science Co. Ltd.).

2. Water contact angle measurement

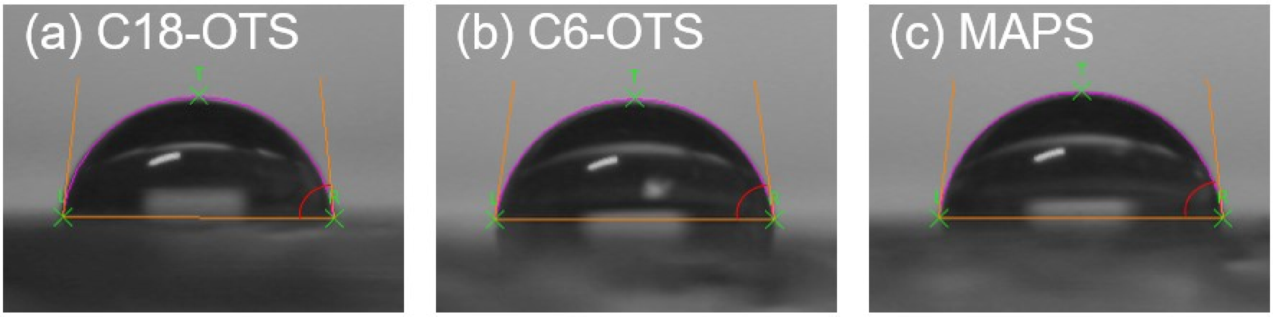

Fig. S1. Photographs of water droplet on (a) C18-OTS-, (b) C6-OTS-, and (c) MAPS-treated ZnO films.

3. Fabrication of ZnO-based memory devices

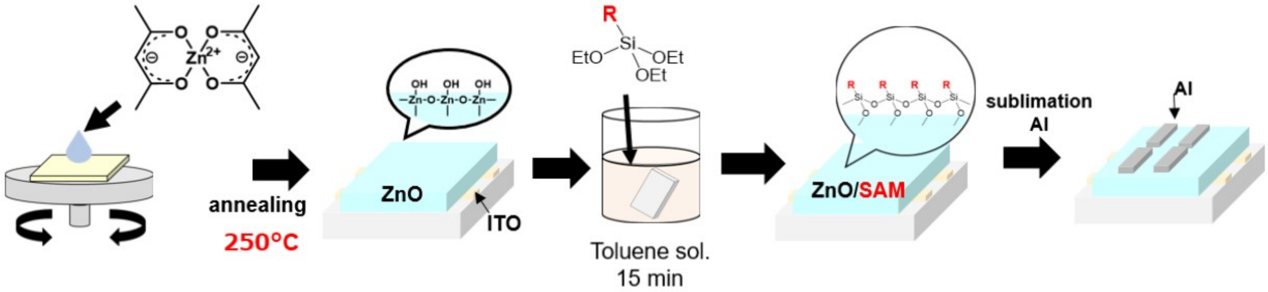

Fig. S2. Fabrication of ZnO-based memory devices.

4. Mechanism of resistive swiching behaviour of ZnO-based memory devices

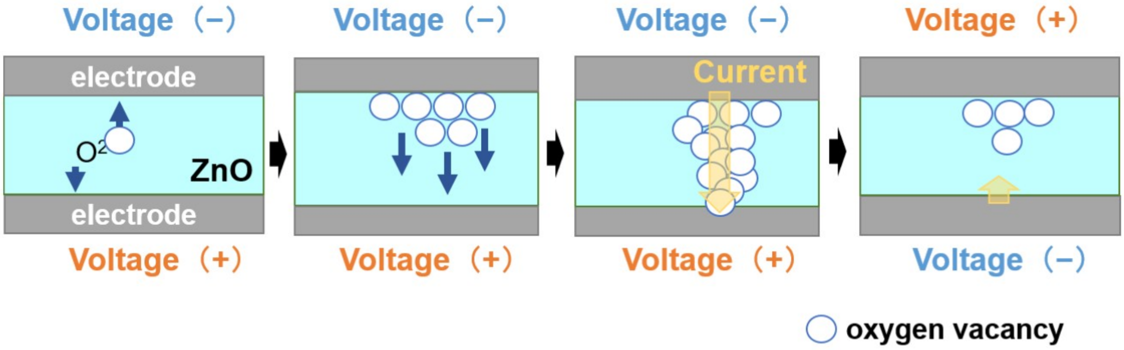

Figure S3. Schematic of mechanism of resistive switching behavior of ZnO-based memory devices.

5. Durability of the ON and OFF states of the ZnO-based memories

The durability of the ON and OFF states of the ZnO-based memory devices under an electrical stress was studied by subjecting the device to a continuous read pulse (1 V, 1 s) every 2 minutes for 12 h with the device in the OFF-state and then in the ON-state.[1] The OFF to ON state transition was obtained by the application of a 4.0 V pulse for the bare ZnO-based device and 2.7 V pulse for the MAPS-treated device.

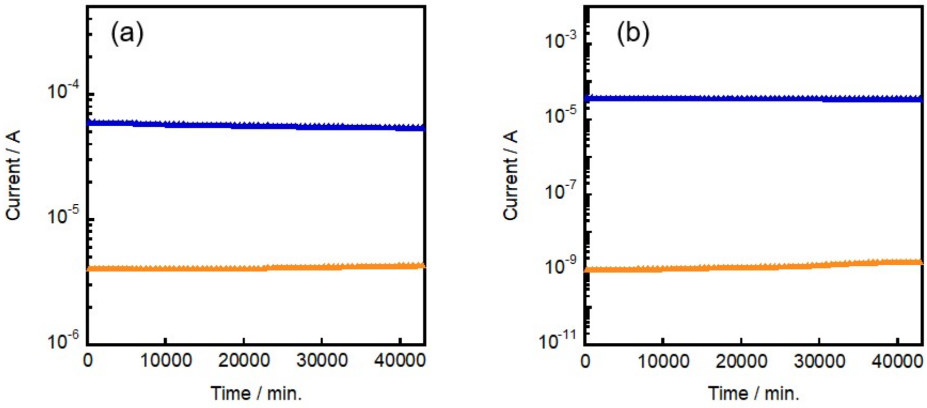

Figure S4. Durability of the ON and OFF states of bare ZnO- (a) and MAPS-treated ZnO- (b) based devices.

6. Retention data of the ZnO-based memories

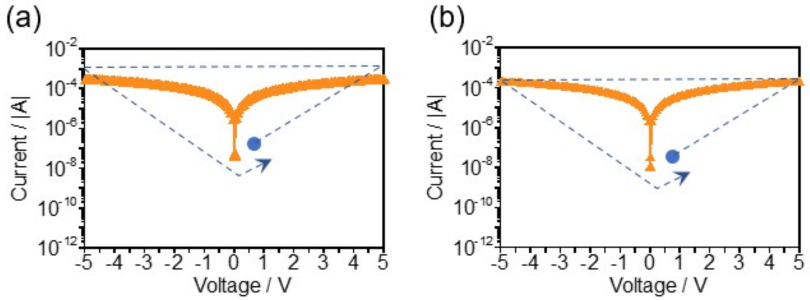

Figure S5. Cycle I-V properties of bare ZnO- (a) and MAPS-treated ZnO- (b) based devices (0 V to 5 V, back to −5 V, and again to 0 V, the second, third, and fourth cycles).

7. ZnO-based memory device with evaporated Al under 10^{-2} Pa.

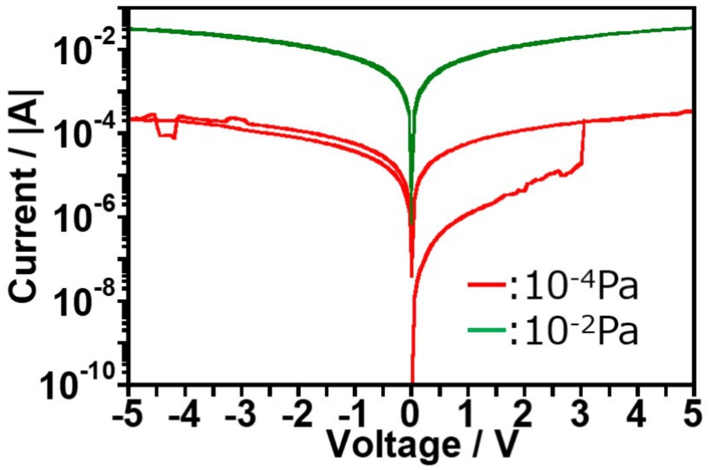

Figure S6. Current-voltage curves of ZnO-based memory device with evaporated Al under 10^{-4} and 10^{-2} Pa.

8. Sparse MAPS-modified ZnO-based memory device

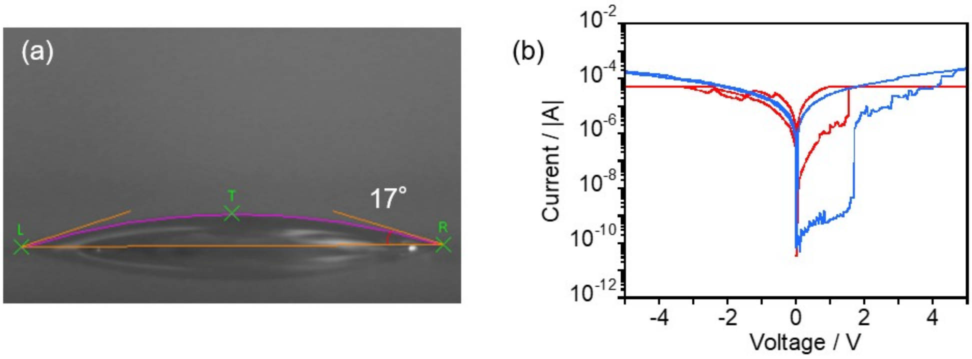

Figure S7. Contact angle measurement of sparse MAPS-SAMs on ZnO (a). Current-voltage curves of sparse MAPS-modified ZnO-based memory device (red trace) and dense MAPS-modified device (blue trace).

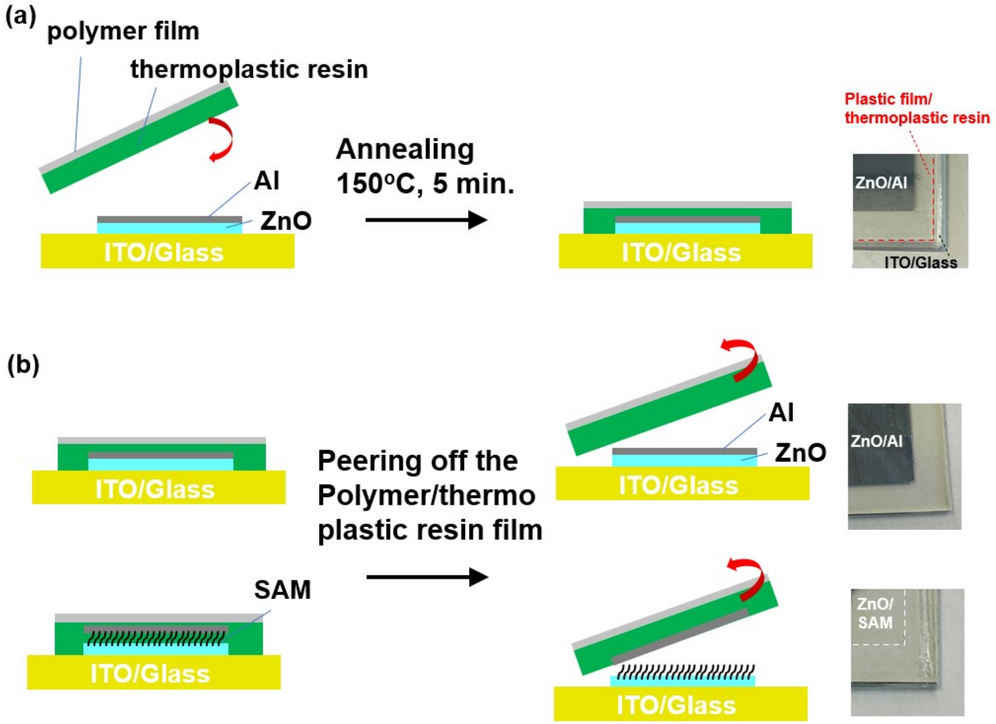

Figure S8. Illustration and pictures of the removing method of evaporated aluminum films from the ZnO-based devices[2] (lamination of polymer/thermoplastic resin film on (a) and removing of aluminum films from the ZnO with and without SAMs (b)).

9. References

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2. T. Fujinuki, M. Nakano, L. Wang, M. Shahiduzzaman, M. Karakawa, T. Taima, *Synth. Met.* **2022**, *285*, 117024.