

Electronic supplementary information (ESI)

**Self-assembled monolayers induced inter-conversion of crystal structure by
vertical to lateral growth of aluminum doped zinc oxide thin films**

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Experimental details: Glass substrates used for the deposition were Eagle 2000 type from Corning. They were cut into (2 x 1) cm² pieces. *n*-Propyltriethoxysilane (H₃C-SAM, 97%, Aldrich), 3-Aminopropyltriethoxysilane (H₂N-SAM, 99%, Acros), and (3,3,3-Trifluoropropyl)trimethoxysilane (F₃C-SAM, 97% , Alfa Aesar) were used as received. Acetone, 2-propanol, and decane were purchased from Acros Organics and were of either semiconductor or reagent grade (99%).

The glass substrates were degreased in a dilute detergent solution followed by sonication in an ultrasonic bath using successive solvents: deionized water (DI water), acetone, and 2-propanol (IPA). Afterwards, the glass substrates were immersed in 0.5 mM solutions of respective SAM forming molecules (H₃C-SAM, H₂N-SAM, and F₃C-SAM) in decane for 24 h. All glass substrates were then removed from the respective solutions and rinsed with plenty of decane and blown dry under constant N₂ flow. The qualities of SAMs were verified by contact angle (CA) and X-ray photoelectron spectroscopic (XPS) measurements.

The AZO films were deposited onto different substrates using a deposition unit with RF plasma sputtering from a ceramic target of 98:2 wt. % ZnO / Al₂O₃ (99.99%, Cathay Advanced Materials Limited), using a plasma power of 40 W. A shutter was placed immediately above the sample to ensure the deposition started only after the equilibrium was reached. Prior to the deposition, the deposition chamber was pumped to a base pressure lower than 1 x 10⁻⁷ Torr, and then back filled with Ar to 13 m Torr. The glass substrates were maintained at room temperature (RT) during entire deposition using a remote temperature controller.

Note: To ascertain the effect of cross-linking, we fabricated AZO films on glass substrates modified with three different SAMs without changing the terminal group (-CH₃): octadecyltrimethoxysilane (OTMS-SAM), octadecyldimethylmethoxysilane (OMMS), and octadecanethiol (ODT-SAM). For the fabrication of ODT-SAM on glass substrate, 10 nm indium doped tin oxide layer was deposited prior to the SAM growth.

Samples were analyzed by X-ray photoelectron spectroscopy (XPS) (VG-Thermo Theta Probe spectrometer) with a monochromated AlK_α as X-ray source. The electrical properties were measured by Van der Pauw method. The optical measurements were performed with a JASCO V-670 UV-Vis spectrometer. The morphology, thickness, and atomic composition of the films were determined using a Field Emission Scanning Electron Microscope (JEOL JSM-6500F), and the crystallinities were investigated by subjecting the samples to X-ray diffraction (XRD) (PANalytical X'Pert PRO). Critical surface tension was measured using Zisman Plot method by a contact angle measurement instrument with three different solvents, namely DI water, ethylene glycol, and hexadecane.

Table S1: Surface tensions of various substrates

Substrates	Bare glass	H ₂ N-SAM on glass	H ₃ C-SAM on glass	F ₃ C-SAM on glass
Surface Tensions $\gamma(\text{mNm}^{-1})$	73.3	27.3	20.4	19.4

Table S2: Contact angles of various substrates

Substrates	H ₂ N-SAM on glass	H ₃ C-SAM on glass	F ₃ C-SAM on glass
Contact angles (degree)	61 ^a	90 ^b	73 ^c

- a. S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Phys. Org. Chem.*, 2001, **14**, 407.
- b. J. L. Lenhart and Wen-li Wu, *Langmuir*, 2003, **19**, 4863.
- c. H. Sugimura, A. Hozumi, T. Kameyama and O. Takai, *Surf. Interface Anal.* 2002, **34**, 550.

Table S3: Contact angles of glass substrates modified with ODT-SAM, OTMS-SAM, and OMMS-SAM.

Substrates	ODT-SAM on ITO/glass	OTMS-SAM on glass	OMMS-SAM on glass
Contact angles (degree)	93.9	94.2	90.4

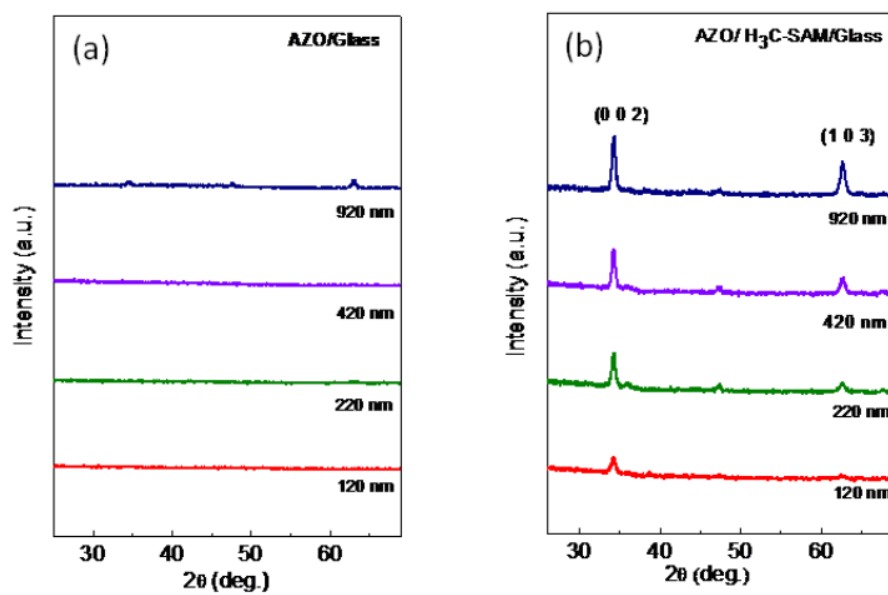


Figure S1. (a) XRD patterns of AZO films at various stages of growth for (a) bare glass and (b) H₃C-SAM modified glass substrates at room temperature.

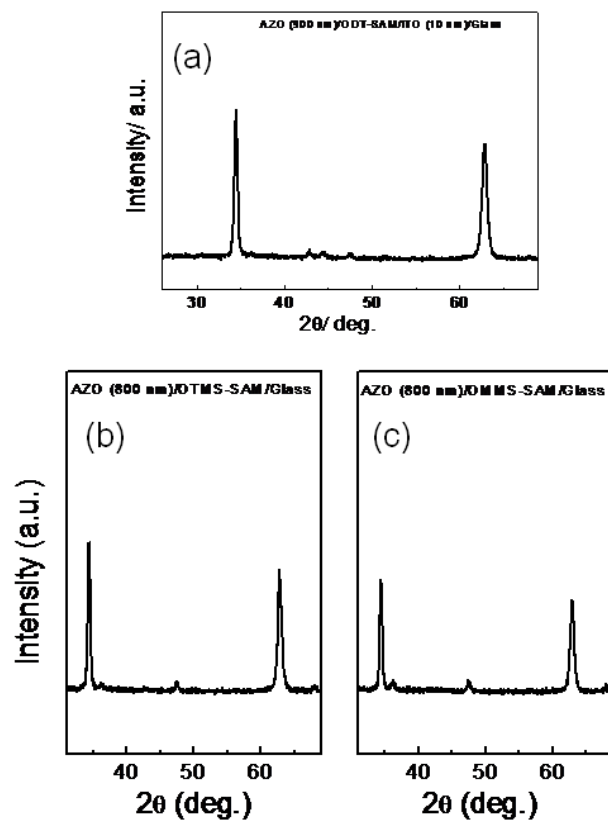


Figure S2. XRD patterns of AZO films deposited at room temperature on various glass substrates modified with (a) ODT-SAM, (b) OTMS-SAM, and (c) OMMS-SAM. The XRD patterns show identical results clearly demonstrating the role of $-\text{CH}_3$ group, irrespective of the nature of SAM forming molecules.

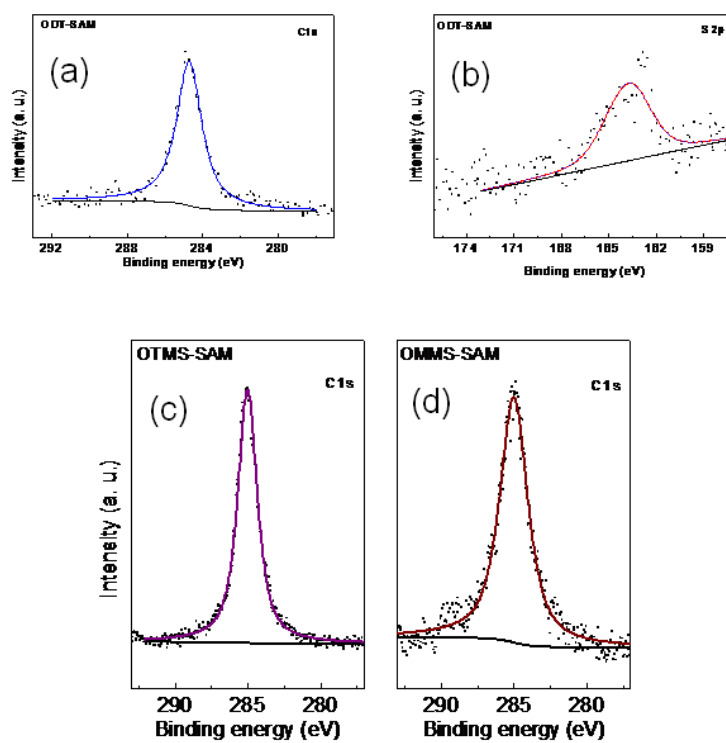


Figure S3. XP spectra of (a) C 1s and (b) S 2p of ODT-SAM and C 1s spectra of (c) OTMS-SAM and (d) OMMS-SAM, respectively.

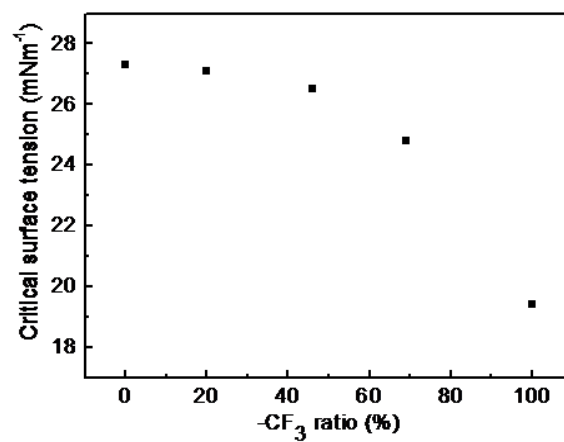


Figure S4. The variation of the critical surface tension against the composition (estimated from XPS spectra) of the ratio (expressed in %) of F₃C-SAM/H₂N-SAM.

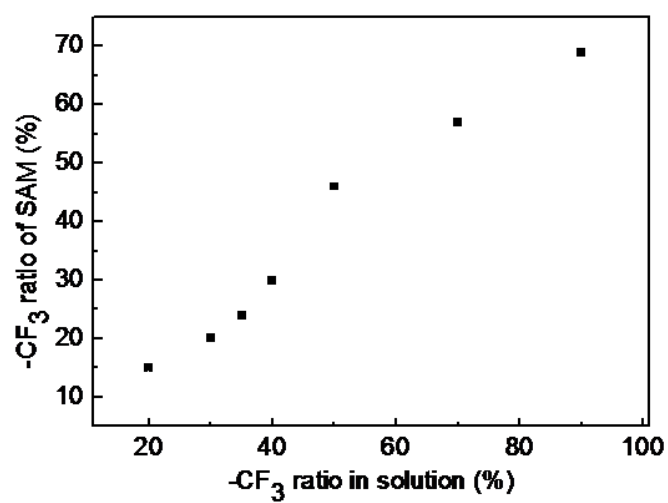


Figure S5. The relationship between the mixing ratio of F₃C-SAM/H₂N-SAM molecules in solution and the real composition (estimated from XPS spectra) of film.

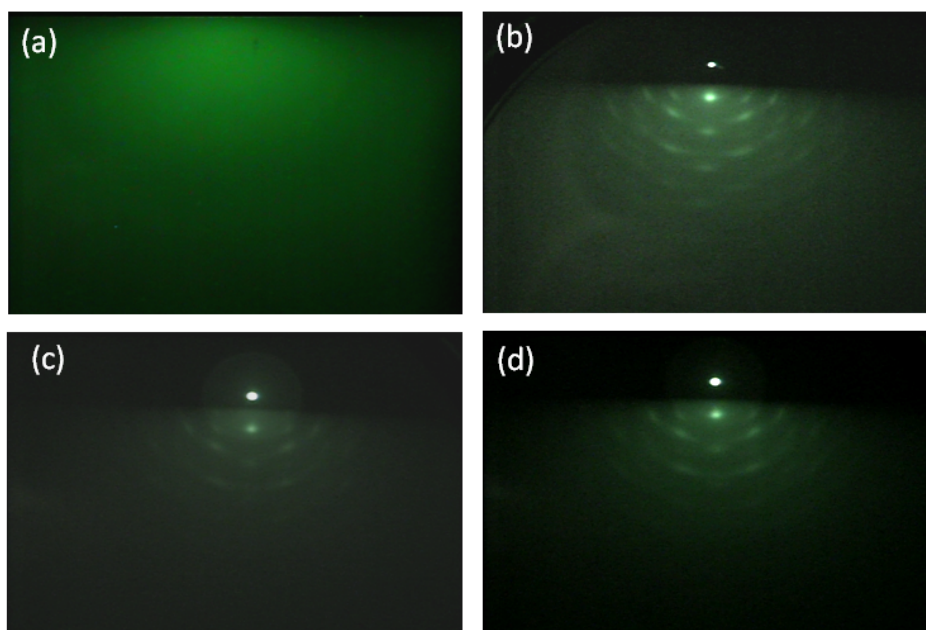


Figure S6. RHEED patterns of AZO films (thickness ~ 720 nm) deposited on (a) bare glass, (b) F₃C-SAM, (c) H₂N-SAM, and (d) H₃C-SAM modified glass substrates.

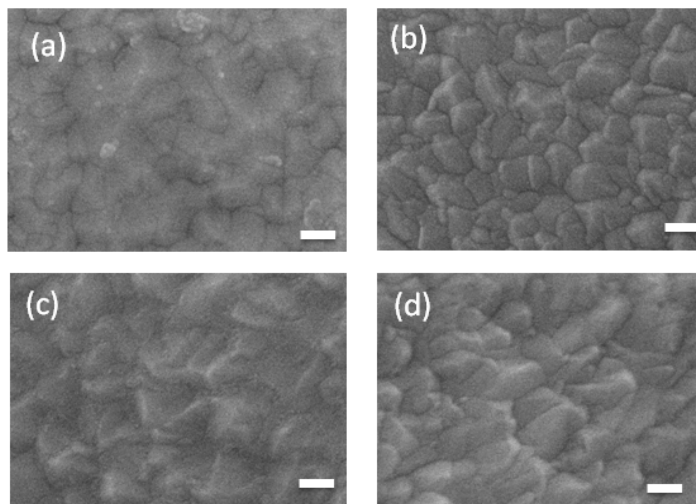


Figure S7. SEM images of AZO films (thickness 920 nm) deposited on (a) bare glass, (b) F₃C-SAM, (c) H₃C-SAM, and (d) H₂N-SAM modified glass substrates. Scale bar is 100 nm.

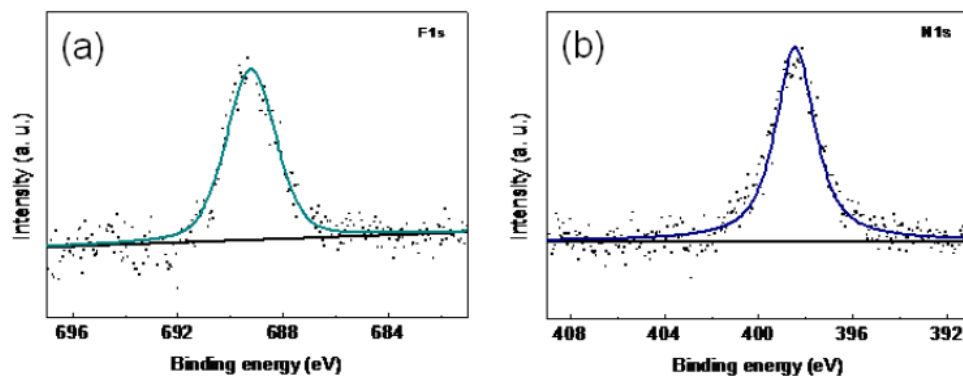


Figure S8. XP spectra of (a) F 1s (B. E. 689.1 eV) and (b) N 1s (B. E. 398.4 eV) electrons for the mixed SAM on a glass substrate. Calculation shows 15 % of $-\text{CF}_3$ groups on the surface for the mixture of F_3C -SAM and H_2N -SAM.

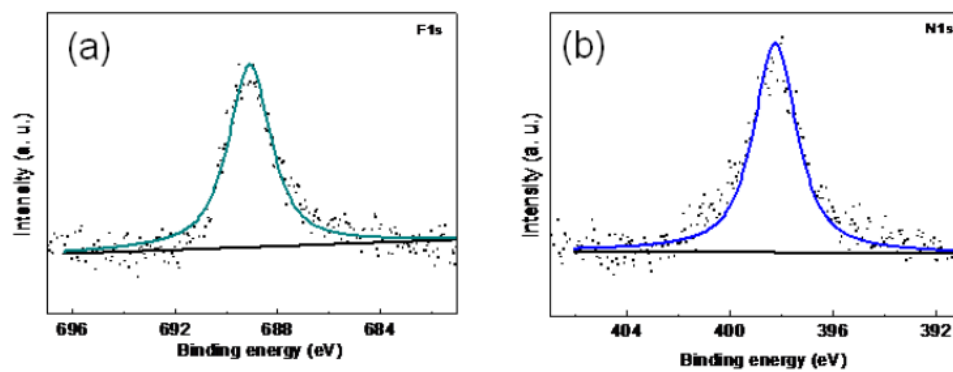


Figure S9. XPS spectra of (a) F 1s (B. E. 689.1 eV) and (b) N 1s (B. E. 398.3 eV) electrons for the mixed SAM on a glass substrate. Calculation shows 22 % of $-\text{CF}_3$ groups on the surface for the mixture of F_3C -SAM and H_2N -SAM.

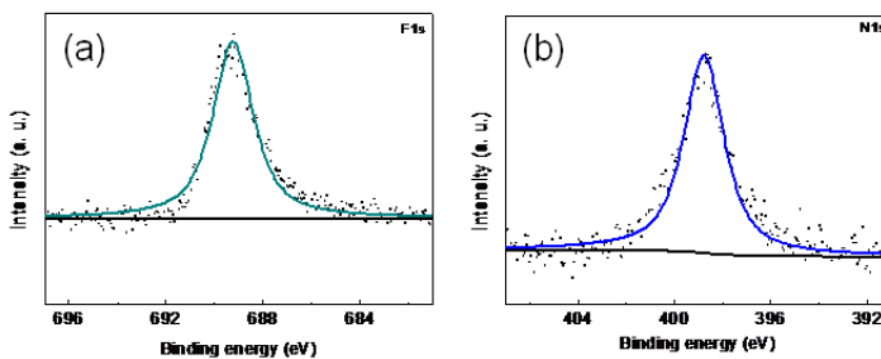


Figure S10. XPS spectra of (a) F 1s (B. E. 689.3 eV) and (b) N 1s (B. E. 398.7 eV) electrons for the mixed SAM on a glass substrate. Calculation shows 35 % of $-\text{CF}_3$ groups on the surface for the mixture of F_3C -SAM and H_2N -SAM.

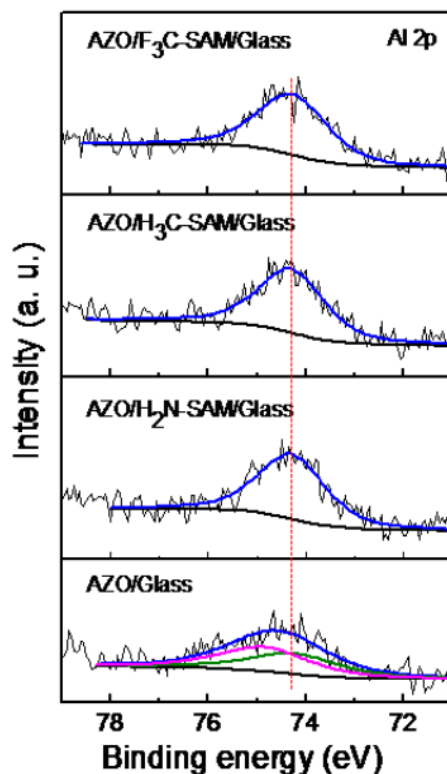


Figure S11. XP spectra of Al 2p electrons for AZO films on various substrates at the initial stages of growth (film thickness 5 nm).

Note: No Al 2p peak for metallic Al (72.9 eV) is observed. Al 2p peaks for AZO films on various SAM modified glass substrates give a binding energy (B. E.) value of 74.3 eV, which indicates replacement of Zn^{2+} ions in the ZnO lattice structure. Al 2p peak for the AZO film on a bare glass substrate gives B. E. value of 74.8 (major peak) and 74.3 (minor peak) eV, which indicates the presence of majority of Al^{3+} ions in the interstitial sites or as pure Al_2O_3 [Y-S. Kim and W-P. Tai, *Applied Surface Science*, 2007, **253**, 4911]. The above results are in good agreement with the electrical properties of various AZO films.