

Supporting Information

Study of Local Band Bending in n-Channel In₂O₃ Thin-Film Transistors Under Gate and Drain Voltage Stress Using *Operando* Hard X-ray Photoelectron Spectroscopy

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The purpose of this supporting information is to present some additional experimental data related to our article on the Study of Local Band Bending and Chemical Change of n-Channel In₂O₃ Thin-Film Transistor Under Gate and Source Voltage Stress By Using *Operando* Hard X-ray Photoelectron Spectroscopy). This work focuses on the chemical change of In₂O₃ Thin-Film Transistor (TFT) induced by both the gate voltage (V_{GS}) and drain voltage (V_{DS}). Fig. S1 (a-b) shows the optical images of our narrow and wide In₂O₃-TFT, respectively. Using the atomic layer deposition In₂O₃ film as a channel layer, top-contact In₂O₃-TFTs were fabricated by depositing 5/150 nm thick Ti/Au electrodes on top of the In₂O₃-channel layer using electron beam evaporation through a shadow mask, forming the source and drain electrodes. It is observed that the In₂O₃ channels are well positioned between the Source/Drain electrodes. Fig. S2 and Fig. S3 report the current-voltage (I-V) characteristics of the In₂O₃-TFT recorded during the chemical analysis of the drain (spot II) and source (spot III), respectively, as reported in Figure 2 (b) from the main manuscript. The I-V data in Figure 3 were obtained in a static mode (fixed voltage for each step). The (a) label illustrates the current I_{DS} versus V_{DS} while sweeping V_{GS} at 0 V, 30 V, 100 V, and -20 V, and the (b) label shows the current I_{GS} versus V_{GS} with V_{DS} set to 0 V and +10 V. This characterization technique is employed here to investigate the In₂O₃ film as well as the buried layers and interfaces under different bias voltage operating conditions. **From Table S1, we report the relative area ratio (%) of each In 3d component from Figure 5(a) from the main manuscript. We underline that from $V_{DS} = 0\text{ V} / V_{GS} = 0\text{ V}$ to $V_{DS} = 0\text{ V} / V_{GS} = 100\text{ V}$, the In⁰ (Red) increases from 0 % to 4 % at a fixed binding energy position (maximum intensity based on Figure 4 (a) from the main manuscript). From $V_{DS} = 0\text{ V} / V_{GS} = -20\text{ V}$ to $V_{DS} = 10\text{ V} / V_{GS} = -20\text{ V}$, we have released the In⁰ energy position and fixed the maximum intensity (based on Figure 4 (b) from the main manuscript). Finally, at $V_{DS} = -0\text{ V} / V_{GS} = -0\text{ V}$, the In⁰ comes back to its initial position, and we observe a slight appearance of peak shoulder as observed in Figure 5 (a) at $V_{DS} = -0\text{ V} / V_{GS} = -0\text{ V}$ from the main manuscript.** In Fig. S4, we report Si 2s, In 4s, and Al 2s core levels shift and broadening, which are consistent with the Si 2p_{3/2}, Al 1s, and In 3d data from the main manuscript. From the Si 2s, we observe how the increase of V_{GS} affects the silicon shape and leads to a huge broadening of the core level. In Fig. S5, we show the integrated area as the function of V_{GS} and V_{DS} recorded from the center of the TFT. we observed that at $V_{GS} = -20\text{ V}$ and $V_{DS} = 10\text{ V}$, the In 3d highlights a splitting phase due to the polarization. In Fig. S6, we report additional HAXPES data from a similar In₂O₃-TFT with a narrow 70 μm length channel. In 3d, Al 1s, Si 2p_{3/2}, and O 1s core levels were obtained around the center of the narrow channel. These data are consistent with the results in Figure 4 in the main manuscript, confirming our measurement's reproducibility. Furthermore, with Fig. S7 and Fig. S8, we respectively present an extended Al 1s and Si 2p_{3/2} core-level analysis from the 130 μm length channel (complementary data to Figure 7 in the main manuscript) at various X-ray beam positions and under different V_{GS} (0 V, 30 V, 100 V, and -20 V) and V_{DS} (0 V and +10 V) configurations. This position-dependent investigation (drain side, center, and source side) enables us to evaluate chemical changes along the channels horizontal direction of the L/W (130 μm / 500 μm) thin film transistor. These data were obtained during the measurement of In 3d from Figure 7 in the main manuscript. From Fig. S9, a schematic description of the photoelectron transport process through the upper stacked layer under applied V_{DS} is presented. By applying a bias along the drain-source direction, we assume a change of the binding energy (BE) of Al 1s and Si 2p_{3/2} photoelectrons from initial BE_i to the final $BE_f = BE_i + \alpha(x) V_{DS}$ when crossing the Al₂O₃/In₂O₃ interface. Since In₂O₃ is a semiconductor, we expect that the potential will be constant from the Al₂O₃/In₂O₃ interface to

the In_2O_3 surface. Therefore, no additional binding energy change will occur inside the channel for a constant (x) position ($\alpha(x)$ constant) along the channel length. However, by moving the X-ray beam from the drain side to the source side, we expect a variation of the $\alpha(x)$ and therefore BE_f . Due to the modification of the potential (ACS Appl. Mater. Interfaces 2016, 8, 38, 2563125636, 10.1021/acsami.6b10332) along the x-axis. Finally, with Fig. S10, we investigate the underneath source/drain electrodes by using thinner Au/Ti (5nm / 5 nm) stacks. Results point out similar trends of In 3d. Conversely to the In 3d data from the channel, under the Au/Ti electrodes, we underline a progressive reduction of the In_2O_3 underneath the source/drain over the measurement time. This result suggests an impact of the Ti/ In_2O_3 interface on the chemical change of In_2O_3 . We also note that except for the presence of the In^0 , no binding energy shift was observed under V_{GS} and V_{DS} . **The progressive variation of the In^0 , In_2O_3 and $\text{In}(\text{OH})_x$ relative area ratio under V_{DS} and V_{GS} is also reported in Fig. S10(c). These quantitative results show that the In^0 goes from 10 to around 30% with the applied bias voltages.**

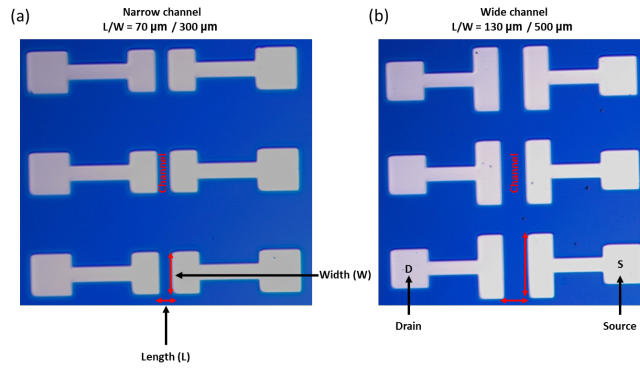


Figure S1: Optical microscopy images of the (a) narrow and (b) wide channel of In_2O_3 thin-film transistors (TFTs) with Au/Ti source and drain electrode.

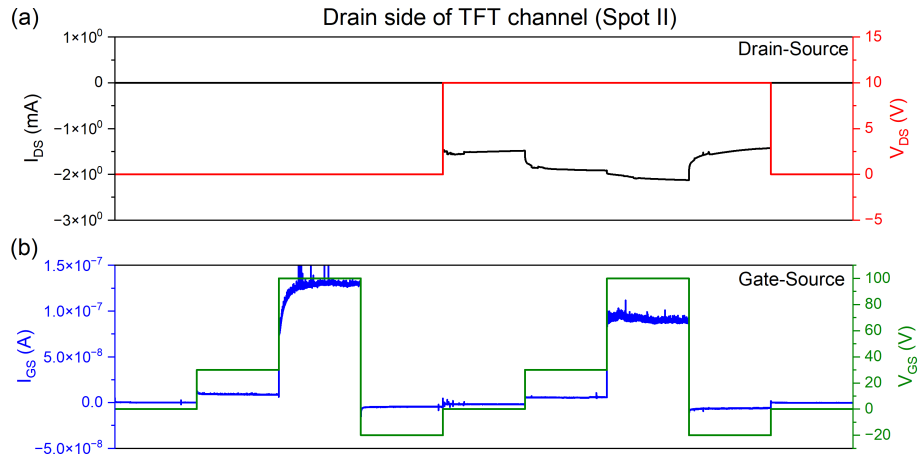


Figure S2: Operando-HAXPES analysis at spot II (drain side of $130 \mu\text{m}$ length channel TFT): (a) IDS-time curve for different drain-source ($V_{DS} = 0\text{V}$ and 10V) voltages, (b) IGS-time curve for different drain-source ($V_{GS} = 0\text{V}$, 30V , 100V and -20V) voltages.

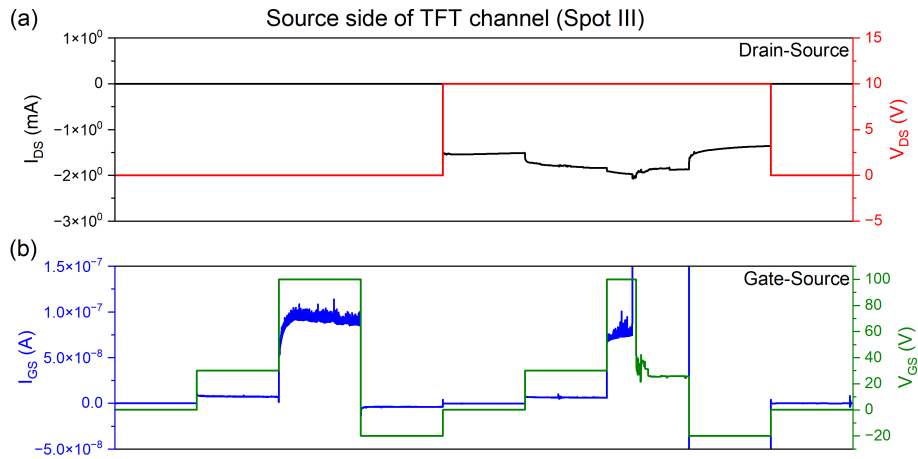


Figure S3: Operando-HAXPES analysis at spot III (Source side of $130 \mu\text{m}$ length channel TFT): (a) IDS-time curve for different drain-source ($V_{DS} = 0\text{V}$ and 10V) voltages, (b) IGS-time curve for different drain-source ($V_{GS} = 0\text{V}$, 30V , 100V and -20V) voltages.

Table S1: Quantitative peak fitting of the In 3d core level spectra to distinguish components evolution under varying applied V_{DS} and V_{GS} bias voltage conditions

Components (%)	Binding energy (eV) as function of the V_{DS} / V_{GS} (Volt / Volt)								
	0 / 0	0 / 30	0 / 100	0 / -20	10 / 0	10 / 30	10 / 100	10 / -20	-0 / -0
In ⁰ (Red)	0	1.3	4	4	4	4	4	4	4
In ₂ O ₃ (Blue)	85	83.7	81	81	81	81	81	81	81
In-(OH) _x (Yellow)	15	15	15	15	15	15	15	15	15

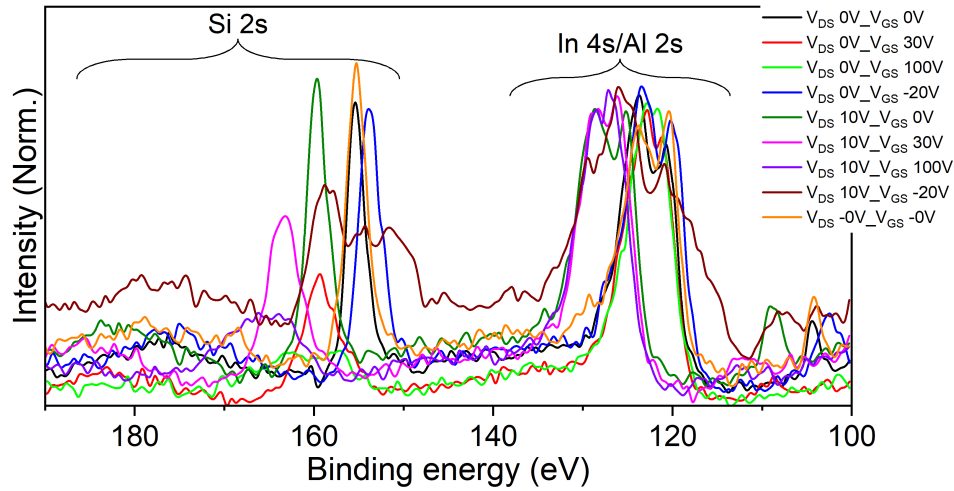


Figure S4: HAXPES spectra of Si 2s and In 4s/Al 2s core level from the center of wide 130 μm length channel from the In₂O₃/Al₂O₃/SiO₂/p⁺-Si thin film transistor under varying V_{GS} and V_{DS} .

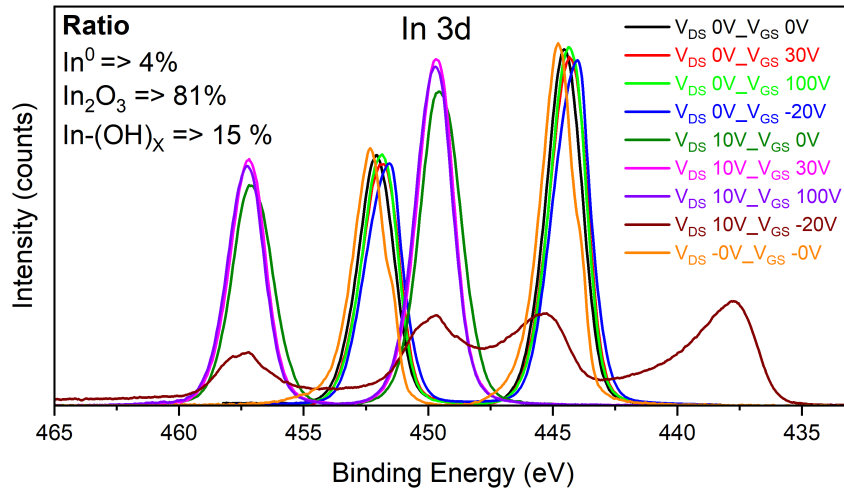


Figure S5: HAXPES spectra of integrated area of In 3d core level from the center of wide 130 μm length channel from the In₂O₃/Al₂O₃/SiO₂/p⁺-Si thin film transistor under varying V_{GS} and V_{DS} .

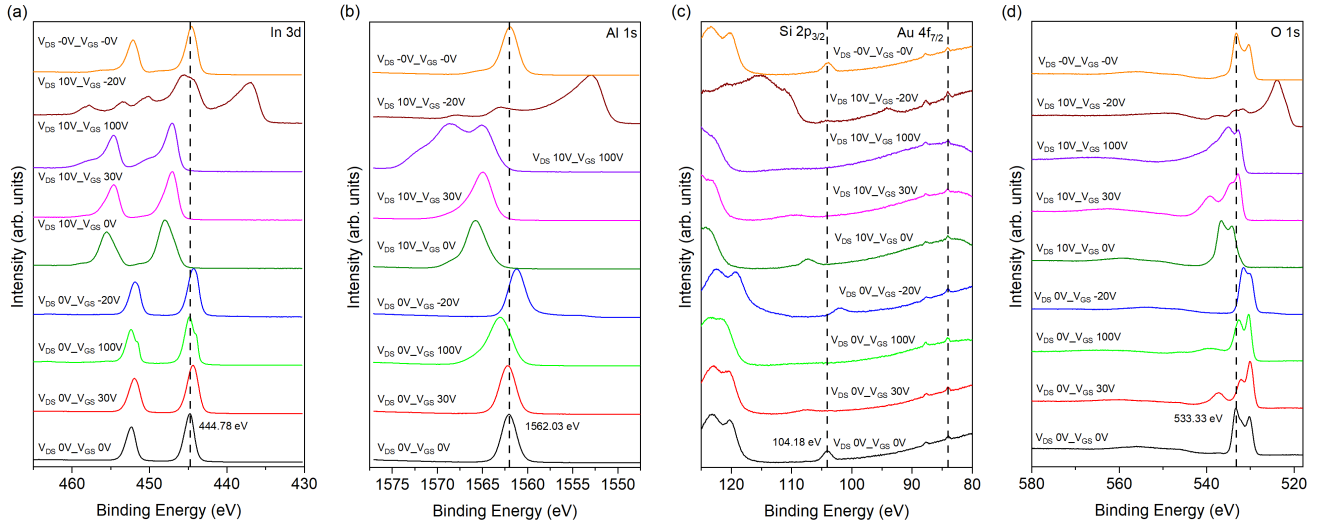


Figure S6: HAXPES spectra of (a) In 3d, (b) Al 1s, (c) Si 2p_{3/2}/Au 4f and (d) O 1s core level from the center of narrow 70 μm length channel from the In₂O₃/Al₂O₃/SiO₂/p⁺-Si thin film transistor under varying V_{GS} and V_{DS} .

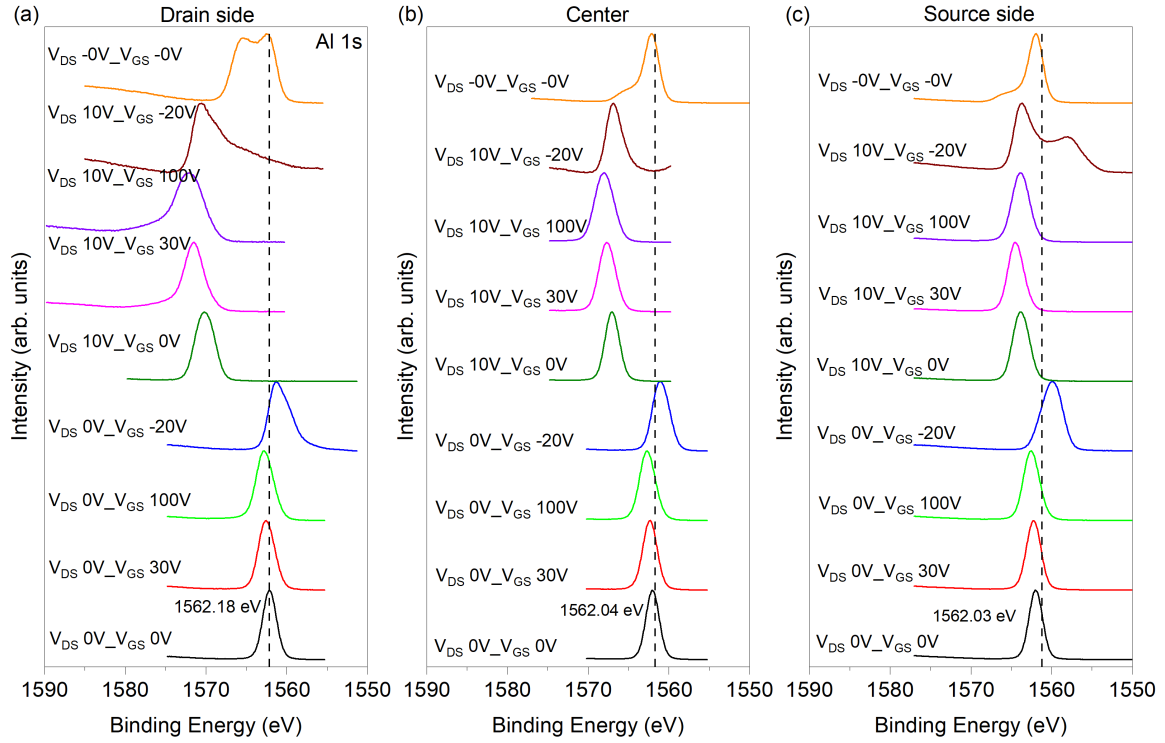


Figure S7: Al 1s core level shifts under varying V_{GS} and V_{DS} : (a) drain side from spot II, (b) center area from spot I, and (c) source side from spot III (130 μm length channel).

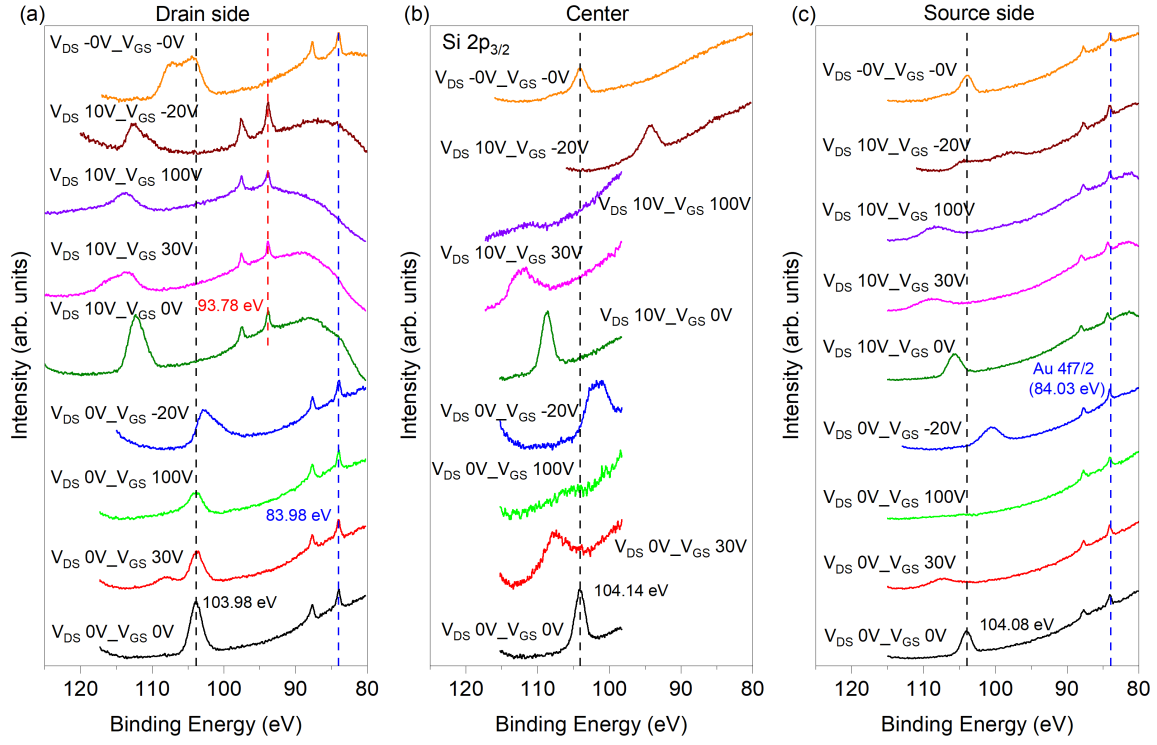


Figure S8: Si 2p (Au 4f) core level shifts under varying V_{GS} and V_{DS} : (a) drain side from spot II, (b) center area from spot I, and (c) source side from spot III (130 μm length channel).

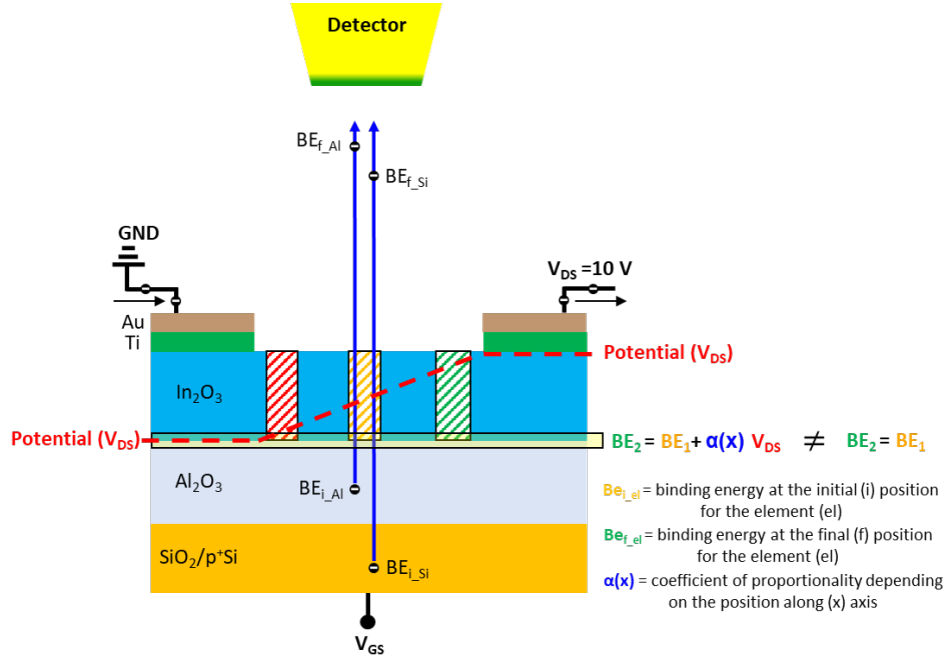


Figure S9: Schematic potential distribution between the drain and the channel electrode at $V_{DS} \neq 0\text{V}$ and the binding energy change of photoemitted electron from the Al_2O_3 and SiO_2 layers when going through the In_2O_3 semiconducting layer.

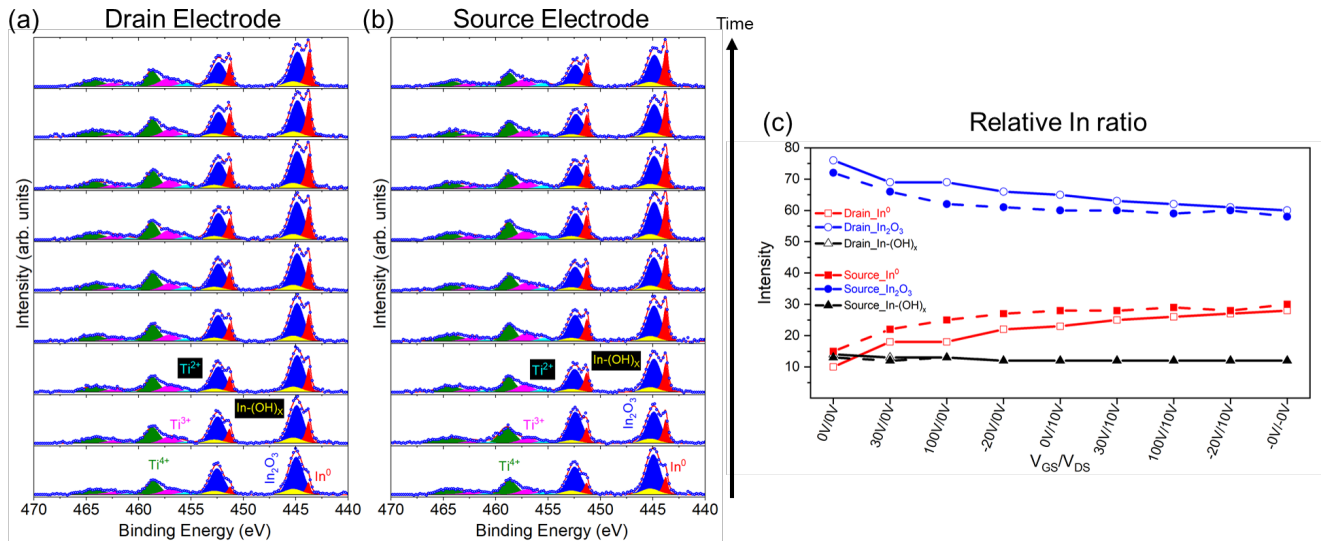


Figure S10: Deconvolution of the In 3d and Ti 2p core levels under varying V_{GS} and V_{DS} on the Au(5 nm)/Ti(5 nm) thin (a) drain, (b) source electrodes of the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{p}^+\text{-Si}$ thin film transistor with a $130\ \mu\text{m}$ length channel. (c) Relative ratio of In^0 , In_2O_3 and $\text{In}(\text{OH})_x$ under varying V_{GS} and V_{DS} .