

Electronic Supplementary Information

Graphene Electrodes Transfer-Printed with a Surface Energy-Mediated Wet PDMS Stamp: Impact of Au Doped-Graphene for High Performance, Soluble Oxide Thin-Film Transistors

Experimental Details

Raw materials: All reagents, DMSO (dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$, 99.9%, Aldrich), zinc acetate dihydrate ($\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, 98%), indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, Aldrich, 99.9%), and gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$, Aldrich, 99.9%), ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, anhydrous 99.8%), formamide (HCONH_2 , Aldrich, >99.5%), monoethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, Aldrich, 99%), and 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, Aldrich, anhydrous 99.8%) were used without additional purification.

Preparation of patterned graphene layers by a wet-PDMS based transfer-printing technique:

For the preparation of graphene sheets, 100 μm -thick Cu foil (from Alfa Aesar) was placed in a quartz tube and heated at 1000 °C under ambient pressure with flowing H_2 and Ar. After the flowing reaction with gas mixtures ($\text{CH}_4:\text{H}_2:\text{Ar}=30:10:1000$ sccm) for 20 min, the sample was cooled to room temperature. The PMMA overcoat layer was spin-coated on top of the graphene sheet, and then the Cu foil was removed by wet etching with a dilute FeCl_3 solution in deionized water. In the case of Au-doped graphene sheets, graphene was additionally immersed into an AuCl_3 aqueous solution with a concentration of 0.025M. Subsequently, the PMMA-coated graphene layer was transferred to a dummy substrate and PMMA was

carefully removed by acetone. When a bilayer graphene sheet was desired, the transfer process was duplicated once more. For facile transfer-printability with a pre-patterned PDMS mold, DMSO diluted in deionized (DI) water (DMSO:DI water = 1:2 in volumetric ratio) was vaporized and coated on the PDMS surface. The PDMS stamp was located 5 cm above a diluted DMSO-water solution at 200 °C for 1 minute. After the contact of PMDS stamp to the graphene-deposited substrate for 1 min, the graphene layer was transferred onto the top-surface of the PDMS stamp. Then, the PDMS stamp was contacted to the surface of the target substrate at 70 °C for 3 min.

Fabrication of soluble-IGZO TFTs employing transfer-printed graphene electrodes: For the preparation of soluble IGZO semiconductors, 0.375 M metal-salt precursors of zinc acetate dihydrate, indium nitrate hydrate, and gallium nitrate hydrate were dissolved in 2-methoxyethanol including either 20 vol% of EG or 50 vol% of FA. The amount of EG or FA was optimized from the viewpoint of device performance and chemical structural evolution.^[13,14] The chemical composition ratio of the IGZO precursor solution was In:Ga:Zn = 63:10:27. Monoethanolamine and DI-water were additionally incorporated as a stabilizer and a reactant for the hydrolysis reaction, respectively. The prepared clear solutions were stirred for 3 hr at room temperature prior to spin coating. For TFTs (bottom-gate, top-contact in a device configuration) with spin-coated IGZO/SiO₂ semiconductor/dielectric stacks, each IGZO precursor solution was spin-coated on a heavily-doped Si substrate with a 100 nm-thick thermal SiO₂ layer. The resulting layers were annealed at 400 °C for 2 hr on a hot plate in air. The source/drain electrodes were formed on top of IGZO semiconductors by printing the bilayer graphene using the wet PMDS-based stamping technique. The channel dimensions were 60 μm in linewidth and 1000 μm in width. For preventing the cleavage of patterned graphene electrodes during measurement with a probe station, the Ag paste was deposited

manually on top of the graphene layer, followed by drying at 120 °C for 10 min. For comparison with a TFT employing conventional thermally-evaporated electrodes, Al source and drain electrodes with 50 nm thickness were deposited via thermal evaporation (pressure $\sim 10^{-6}$ Torr) through shadow masks. The channel length and width were 100 and 1000 μm , respectively. The TFT characteristics were measured using an Agilent 4155C semiconductor parameter analyzer. The saturation mobility and threshold voltage were calculated using the conventional metal-oxide-semiconductor field effect transistor (MOSFET) model.

Characterization: The chemical structure of the graphene layer was examined by X-ray photoelectron spectroscopy (XPS, Omicron, ESCA Probe). The surface XPS data were collected using monochromatic $\text{AlK}\alpha$ radiation (1486.6 eV) in an ultrahigh vacuum system with a base pressure of $\sim 10^{-10}$ Torr. The structure of the graphene layer was characterized by micro Raman spectroscopy (Renishaw, 514 nm, Ar^+ ion laser). The morphology of the patterned graphene layers was investigated by an optical microscope (Nikon OPTIPHOT). The work function of both graphene and IGZO semiconducting layers was analyzed with ultra-violet photoelectron spectroscopy (UPS, AXIS Ultra DLD, KRATOS Inc.) with a He I (21.22eV) source. The typical sheet resistance and transmittance of the graphene films were measured by using a four-point probe (Hall ECOPIA HMS-5000) and ultraviolet–visible (UV-vis) spectroscopy (SHIMADZU, UV-250/PC).

Table S1. Position, the full-width-at-half-maximum (FWHM), and areal fraction of each Au4f XPS band for the Au-doped graphene layer

	Au(0) 4f _{7/2}	Au(0) 4f _{5/2}	Au(III) 4f _{7/2}	Au(III) 4f _{5/2}
Band (eV)	83.7	86.2	87.4	89.9
FWHM (eV)	1.3	1.2	1.2	1.3
% Area	51.3	4.5	40.6	3.6

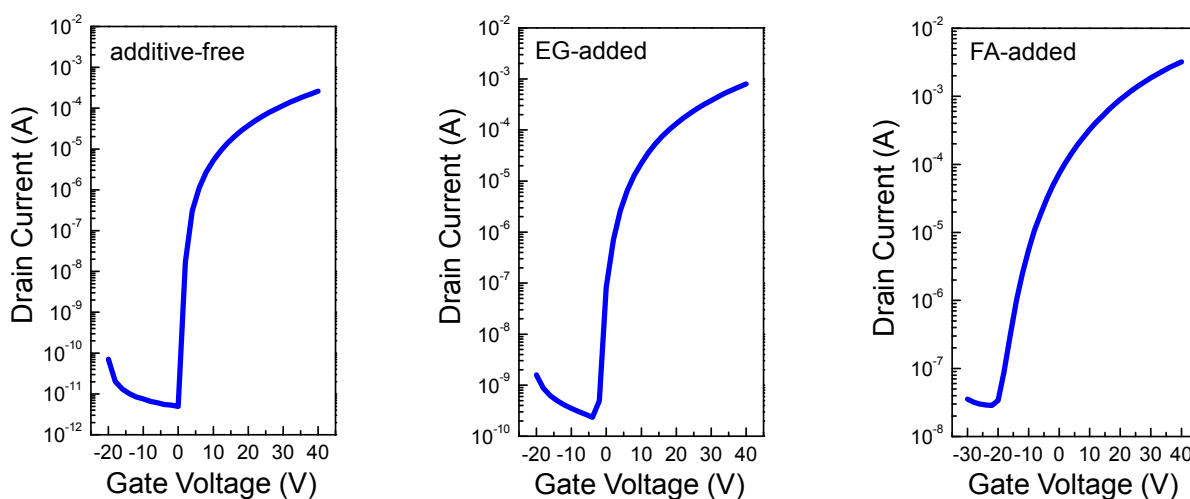


Fig. S1 Transfer characteristics of Al-IGZO TFTs employing a channel layer prepared from additive-free, EG-added, and FA-added precursor solutions.

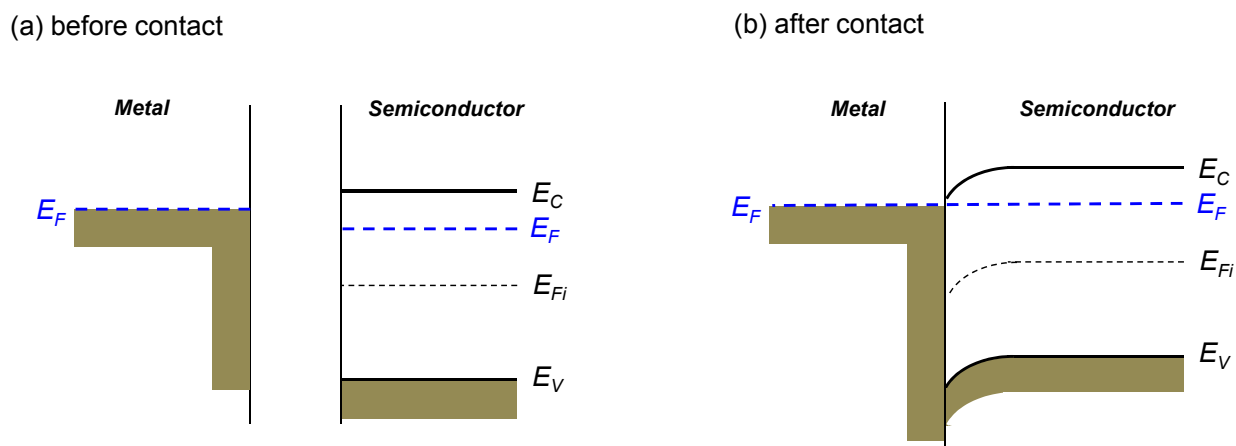


Fig. S2 Schematic diagram of ideal energy band diagram (a) before contact and (b) after contact for a metal/n-type semiconductor junction.

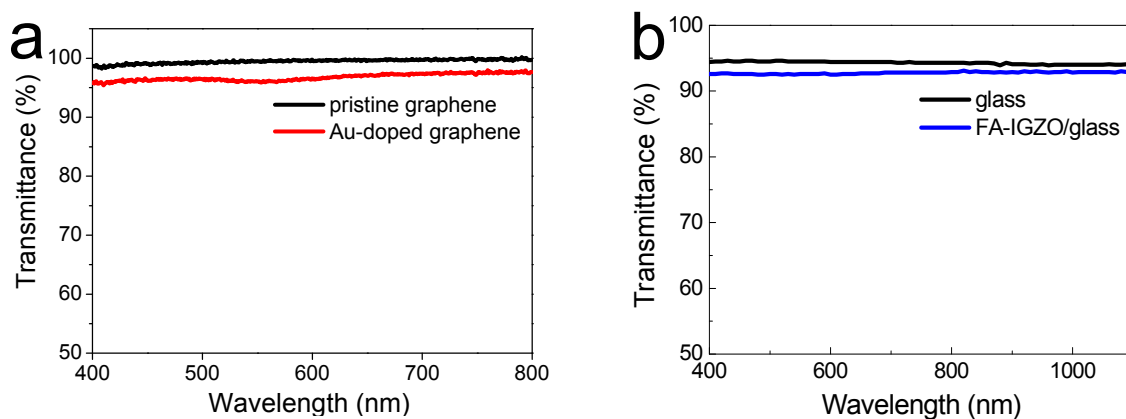


Fig. S3 Transmittance of (a) pristine and Au-doped graphene layer and (b) FA-IGZO semiconductor. The transmittance of the graphene layers was obtained by subtracting the transmittance of the glass substrate, and FA-IGZO was deposited by spin-coating the precursor solution on a glass substrate (annealing temperature: 400 °C).