Flexible Spray-Coated TIPS-Pentacene Organic Thin-Film Transistors as Ammonia Gas Sensors

Xinge Yu^{a,b}, Nanjia Zhou^{b,c}, Shijiao Han^a, Hui Lin^{a,b}, Donald B. Buchholz^c, Junsheng Yu^{a*}, Robert P. H. Chang^{c*}, Tobin J. Marks^{b*}, Antonio Facchetti^{b,d*}

^aState Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of

China (UESTC), Chengdu, 610054, P. R. China

^bDepartment of Chemistry and the Materials Research Center, Northwestern

University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA

^cDepartment of Materials Science and Engineering, the Materials Research Center,

Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA

^dPolyera Corporation, 8045 Lamon Avenue, Skokie, Illinois, 60077, USA

Experimental Section

The OTFTs were fabricated according to the following procedure. The indium tin oxide (ITO) coated glass and ZITO coated AryLite polyester were used as the substrates and the gate electrodes. The ITO coated glass was purchased from commercial sources (Thin Film Devices Inc.), and the amorphous ZITO film having 250 nm thickness was deposited on flexible substrates, AryLite polyester, by pulsed laser deposition (PLD). Here 30% of the ITO In is replaced by Zn and Sn (Zn0.3In1.4Sn0.3O3). The transparency of the ZITO/AryLite polyester substrates is >80 %, the sheet resistance of the ZITO films <20 Ω/\Box , and the mechanical flexibility of these ZITO/AryLite polyester substrates shows an bending radius ~2.5 mm. PMMA (Aldrich, MW~350,000) was selected as the dielectric layer, was dissolved in chlorobenzene to form a 7 % solution after stirring for more than 10 h by stir bar. Then PMMA solution was next spin-coated on ITO/glass and ZITO/AryLite as the dielectric layer, and baked on a hot plate at 150 °C for 1 h. Using a Veeco Dektak 150 surface profiler, the thickness of PMMA film was measured to be ~ 520 nm. Subsequently, Various concentrations of TIPS-pentacene solution, from 2 to 8 mg/mL, were prepared in dichlorobenzene, and deposited via spray coating on the PMMA dielectric layer as the OTFT active layers. After extensive optimization, optimal films were obtained by controlling the spray coating parameters as such the height from the nozzle tip-to-substrate at 15 cm, with a spray pressure of 40 psi using 5 mg/mL solution. The TIPS-pentacene solution was nebulized onto the substrate at a rate 250 μ L/min. The thickness of active layer is ~30 nm as characterized also by the Veeco Dektak 150 surface profiler. Finally, the source and the drain electrodes of 50 nm gold (Au) were thermally evaporated on TIPS-pentacene active layer and patterned with a shadow mask. The device channel width/length ratios are 100 (W=10 mm, L =100 μ m) and 20 (W=1 mm, L =50 μ m). Once the fabrication steps were complete, without surface modification or encapsulation, the devices were characterized with a Keithley 4200 programmable bias-current source.

To evaluate the sensitivity characteristics to NH_3 gas, the OTFT sensor was stored in an airtight test chamber (approximately 50 mL). High-purity nitrogen (N₂) and 500 ppm standard NH_3 gases were mixed in the appropriate concentrations, and then introduced into the test chamber by a mass flow controller (MFC), the corresponding NH_3 concentration varied between 10 ~ 100 ppm. The NH_3 gas response characteristics of the OTFT sensors were measured with the output, transfer characteristics, and the change in the drain/source current variation as a function of time.

Atom force microscopy (AFM) film morphologies were imaged with a Veeco Dimension Icon scanning Probe Microscope in tapping mode. XRD measurements were performed with a Rigaku ATX-G Thin Film Diffraction Workstation using Cu k α radiation coupled to a multilayer mirror.



Figure S1. AFM images of a typical PMMA film used as the gate dielectric: (a) as prepared, (b) after spray-coating with the dichlorobenzene solvent (the spraying parameters are as same as for the TIPS-pentacene solution spray-coating).



Figure S2. Sub-threshold swing (*SS*), and trap density (N_{trap}) of OTFT sensors after exposure to various NH₃ concentrations



Figure S3. Output curves of TIPS-pentacene OTFT sensors after exposure to air for the indicated number of days: (a) devices tested in N₂, (b) devices tested in 100 ppm NH₃ concentration. The gate voltage V_{GS} is -40 V, and the drain voltage V_{DS} ranges from 0 to -40 V. Channel lengths (*L*) and widths (*W*) of these devices are $L = 100 \mu$ m, and W = 10 mm, respectively.



Figure S4. Typical transfer and output curves of the flexible TIPS-pentacene OTFTs with different channel lengths (*L*) and widths (*W*): (a), (b) for a device with $L = 50 \mu m$, and W = 1 mm; (c), (d) for a device with $L = 100 \mu m$, and W = 10 mm. The flexible devices were fabricated on Arylite substrates (250 nm thick ZITO gate electrodes/520 nm PMMA dielectric layer, with 30 nm TIPS-pentacene active layer, and 50 nm Au source/drain electrodes.

Table S1. Relative response $\Delta I_{DS}/I_{DS}$, and recovery time of an OTFT sensor exposed to NH₃ gas in concentrations ranging from 0 to 100 ppm. The data are extracted from Fig. 4(b).

Relative response	Recovery time (s)	
$\Delta I_{DS}/I_{DS}$		
0.25	81	
0.35	114	
0.55	190	
0.83	235	
	Relative response $\Delta I_{DS}/I_{DS}$ 0.250.350.550.83	

NH ₃ concentration	Relative response	Field-effect mobility	Threshold voltage
(ppm)	$\Delta I_{DS}/I_{DS}$	μ (cm ² /Vs)	$V_{\mathrm{T}}\left(\mathrm{V} ight)$
0	-	0.067	-5.9
10	0.21	0.063	-8.7
25	0.34	0.059	-11.2
50	0.48	0.054	-13.5
75	0.54	0.051	-15.6
100	0.59	0.048	-19.1

Table S2. Relative response $\Delta I_{DS}/I_{DS}$, field-effect mobility μ , and threshold voltage V_T , of a flexible OTFT sensor exposed to NH₃ gas in concentrations ranging from 0 to 100 ppm.