

Supporting Information

High Performance Organic Thin-Film Transistors Based on Hexamethylenetetrafulvalene Lying Flat-on-Surface with Non-Layered Packing Motif

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1. Polymer coating

For the substrate, we used n^+ -doped silicon with 500-nm-thick layers of thermally oxidized SiO_2 (6.7 nF/cm^2). For spin-coating by polymers, we used a 0.11 wt% solution of PS in toluene, a 0.8 wt% solution of PC in chlorobenzene, a 0.1 wt% PMMA in toluene, or a 0.11 wt% solution of PVA in water. Before they were spin-coated with the polymer, the substrates were subjected to chemical cleaning, exposure to UV/ozone (SEN Lights Corp., PL16-110), and drying in an oven for one hour at 100°C . The polymer solutions were filtered through a mesh filter ($0.5 \mu\text{m}$ pore size) before use. The surfaces of the polymer coatings were quite smooth; the r.m.s values were 0.35 nm for PS, 0.54 nm for PC, 0.31 nm for PMMA, and 0.44 nm for PVA, compared with 0.14 nm for the substrate. Spectroscopic ellipsometry measurement showed that the capacitances of the polymer-coated substrates were about $0.2\text{--}0.5 \text{ nF/cm}^2$; these values are less than that of the substrate without the polymer layer. The water contact angles are estimated as 92° , 88° , 68° , 46° , and 103° for PS-, PC-, PMMA-, PVA-, and HMDS-treated surfaces, respectively.

2. Device fabrication

TTF–TCNQ charge-transfer complex was obtained by mixing solutions of TTF and TCNQ in acetonitrile. HMTTF (M.W. = 284) was synthesized chemically according to the reported procedure (Greene, R. L.; Mayerle, R.; Schumaker, R.; Castro, C.; Chaikin, P. M.; Etemad, S.; Laplaca, S. J. Solid State Commun. 1976, 20, 943.) and purified by repeated crystallization. Powdered HMTTF was thermally evaporated in vacuum (2×10^{-5} Pa) at a deposition rate of 0.01 nm/s onto the substrates that were kept at room temperature. After about 100 nm thickness deposition of HMTTF layer, TTF–TCNQ source and drain electrodes were deposited in the same chamber by using a shadow mask that was exchanged in the glove box. The lengths of the channels were 100–300 μm and they were 1000 μm wide. All the processing of the devices was performed in a vacuum-deposition chamber integrated with an argon-filled glove box.

3. Characterization

The AFM images were recorded by using a scanning probe microscope (Veeco, Nanoscope IIIa). To evaluate the structure of HMTTF film on various substrates, x-ray diffraction measurements of samples of powder materials scratched off the substrates were performed. HMTTF single crystal, evaporated HMTTF films on the substrates, and polystyrene polymer were brayed and powdered. X-ray diffraction measurements of the powder samples which were placed in a 0.3-mm-diameter capillary tube were performed at the BL-1A line of Photon Factory (KEK, Japan), by using a monochromatized focused beam ($\lambda = 0.6871$ Å) measuring 0.3 mm (vertical) by 0.7 mm (horizontal). The results are shown in Figure 1; the diffraction patterns are roughly identical including the linewidths. It is clear from this that all the film materials are isostructural and have similar film quality.

In contrast to the powder diffractions, intensity of the thin film diffractions measured for the films with a constant thickness of 100 nm is much different with each other, as presented in Figure 3(b) of the main text. These features allow us to estimate the degree of crystallographic orientation of the grains along the b-axis (perpendicular to the substrate) from the relative intensities of (040) peaks.

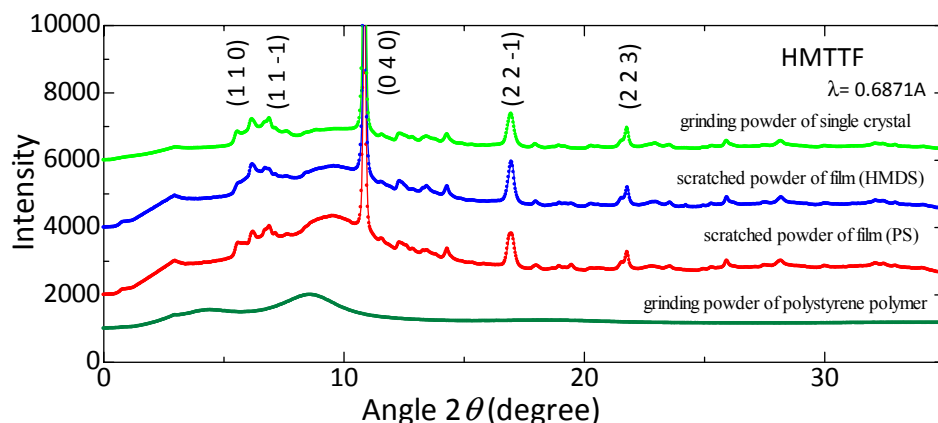


Figure. 1 X-ray powder diffraction pattern of materials scratched off the substrates with variously modified surfaces.

4. Stability of the Device

The dc field-effect characteristics of all the devices were measured under inert gas in an argon-filled glove box with probes attached to a parametric analyzer (Agilent, E5270A). When kept under inert atmosphere, the device fabricated on the PS-treated substrate showed a performance that was stable and reproducible during several days. From the slope of the transfer curves, the mobility in the linear region is estimated to be $6.9 \text{ cm}^2/\text{Vs}$ in the forward sweep and $2.3 \text{ cm}^2/\text{Vs}$ in the backward sweep. Under atmospheric conditions, however, the performance rapidly degraded by about one-order of magnitude to a value of about $0.66 \text{ cm}^2/\text{Vs}$, although it subsequently became quite stable for at least several weeks and the nonlinearity and the hysteresis becomes negligible as plotted in the figure.

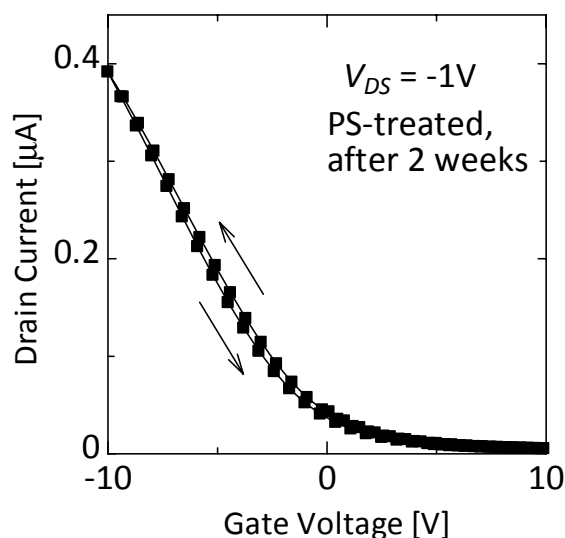


Figure. 2 Transfer characteristics of HMTTF OTFTs on a PS-treated substrate after two weeks under atmospheric conditions.