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Reduced crystallinity and enhanced charge transport by melt annealing of an organic semiconductor/graphene bi-layer†

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Supplementary Information

Graphene layer preparation

Large-area single layer graphene samples were synthesized on a copper foil by chemical vapour deposition (CVD) using a vertical quartz tube.[1] The copper foil was pre-treated in acetic acid for at least 30 minutes in order to smoothen the ridges of the foil. This step is necessary to minimize structural defects during the graphene growth by forming less nucleation sites.[2] This step was followed by a brief cleaning in acetone and isopropanol. Next, the copper foil was annealed for 90 minutes in a flow of 10 sccm H_2 at 120 Torr. A flow of 0.15 sccm CH_4 was introduced for 30 minutes while maintaining the same H_2 flow. Subsequently, the tube was removed from the oven and cooled rapidly to room temperature under H_2 flow. The graphene layer on copper was characterized by Raman, which shows full monolayer coverage.[3] The sample was then spin-coated with poly(methyl methacrylate) (PMMA), and the copper was etched in ammonium persulfate. Once fully etched, the graphene was placed in a 10% HCl solution for 10 mins in order to remove remaining Cu residues. Finally, the graphene was transferred into DI water before being placed onto a substrate. The transfer of graphene onto hydrophobic substrates is more challenging compared to conventional hydrophilic substrates like SiO_2/Si and glass.[4] For a successful transfer, diluted isopropanol (IPA) was used in order to reduce the repulsive force between the liquid and the substrate. A mixture of 35 mL of DI water and 15 mL of IPA helps minimize the repulsion between the liquid and substrate. It provides enough surface tension to keep the graphene floating and to prevent the graphene from wrinkling. The hydrophobic substrate was placed at the bottom of the beaker, and the water was slowly removed in order to let the graphene settle onto the substrate. The sample was dried overnight before removing the PMMA with acetone.

P3HT film preparation

A freshly prepared solution of P3HT 1.7% (mass.) in o-dichlorobenzene was filtered through a syringe filter (pore size 0.45 μm) and used for the film deposition. The thin P3HT films on graphene-coated silicon (graphene/Si) were prepared by spin coating at 1000 revolutions per minute (rpm) for 150 s (until the films were dry), resulting in films of $\approx$ 85 nm thick. The films were then annealed in inert nitrogen atmosphere at 200° C or 240° C for 15 min, followed by slow cooling (1°/min) to room temperature.

Flexible electrodes for conductivity measurement

The vertical conductivity of the P3HT samples was characterized with home-made smooth and planar flexible electrodes. The liquid Polydimethylsiloxane (PDMS) was mixed on a 10:1 ratio with its curing agent, poured onto a smooth hexamethyldisilazane (HMDS)-treated silicon wafer and cured at a temperature of 150°C for at least five hours. The formed smooth PDMS stamp was covered with 150 nm silver layer using Kurt Lesker PVD 75 evaporation deposition system. The current was measured vertically from the bottom of the conductive Si substrate to the top of the films. Polydimethylsiloxane (PDMS) was purchased from Dow Corning Corp. (Sylgard ® 184), hexamethyldisilazane (HMDS) was purchased from Sigma-Aldrich. The current-voltage (I-U) characteristics were collected with a Keithley 2400 source meter. The exact surface areas of the flexible top electrodes were estimated by optical microscopy and were used for the calculation of the current density.

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† Electronic Supplementary Information (ESI) available: Experimental procedures for preparation and characterization of the samples. See DOI: 10.1039/b000000x/

Characterization by grazing incidence X-ray diffraction

Grazing incidence wide-angle X-ray diffraction (GIXD) experiments were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11–3 (2D scattering using an area detector, MAR345 image plate), and on beamline 2–1 (out-of-plane X-ray diffraction) using a point detector, and the same incidence energy and angle. The X-ray beam energy was 12.7 keV, and the incident angle α was either 0.13° in order to probe the whole thickness of the P3HT films or 0.08° in order to probe the topmost layer of the P3HT films. All the diffraction experiments were in an helium-filled chamber in order to reduce background scattering and avoid sample damage by the beam. Several spots were measured on each sample, and showed very good reproducibility. The beam penetration depth was calculated using the approach of Henke et al.[5] For the incidence angle of 0.13° , the beam penetration depth equals $\approx 2.36\ \mu$m, and for the incidence angle of 0.08° , only the top 10 nm are probed.

The 2D GIXD datafiles (*.mar2300) were analysed using the WxDiff software. In particular, the xy cross-sections were extracted and normalized by the X-ray beam intensity Monitor value. The diffraction intensities and crystallographic parameters were estimated via analysing the 100 and 010 peaks on the background-corrected curves located at the values of the scattering vector length $q \approx 0.4$ and $1.6\ ^{-1}$. The peak centre locations were estimated via interpolating the corresponding peaks with Gaussian function and calculating the d-spacings using the Braggs' equation. Pole figure plots (I = f(χ)) were built for the 100 and 010 peaks using the integrated peak intensity value for every polar angle between 0 and 90 degrees. Due to the curvature of the Evald sphere, the data below 2° χ in the case of (100) peak and below 8° χ in the case of (010) peak was not taken into account.

References

1 D. R. Cooper, B. D'Anjou, N. Ghattamaneni, B. Harack, M. Hilke, A. Horth, N. Majlis, M. Massicotte, L. Vandsburger, E. Whiteway and V. Yu, *ISRN Condens. Matter Phys.*, 2012, **2012**, 501686.

2 M. Massicotte, V. Yu, E. Whiteway, D. Vatnik and M. Hilke, *Nanotechnology*, 2013, **24**, 325601.

3 V. Yu, E. Whiteway, J. Maassen and M. Hilke, *Phys. Rev. B*, 2011, **84**, 205407.

4 S. Bernard, E. Whiteway, V. Yu, D. G. Austing and M. Hilke, *Phys. Rev. B*, 2012, **86**, 085409.

5 B. Henke, E. Gullikson and J. Davis, *Atomic Data and Nuclear Data Tables*, 1993, **54**, 181 – 342.