Electronic Supporting Information

Ordered Ionic Liquid Structure Observed at Terraced Graphite Interfaces

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Experimental methods

Deposition of Ionic Liquid Ultrathin Films

[EMIM][Tf_2N] of ultrapure quality with a halide concentration below 50 ppm was purchased from Ionic Liquids Technologies Inc. (IoLiTec). The IL was loaded into a 10-mL crucible in a nitrogen-filled glovebox, and the crucible was attached to a low-temperature effusion cell with a top-down evaporation geometry (SVT Associates, Inc.) for the preparation of IL films. Prior to vapor deposition, the IL was degassed under low and high vacuum until a base pressure of $<10^{-7}$ mbar was reached; it was slowly heated to above 400 K to further reduce volatile impurities such as the water content. Evaporation of the IL was made at 430 K, far below its decomposition temperature.[1-4] By controlling the deposition time, ultrathin IL films of different thickness were prepared on selected carbon substrate surfaces (HOPG, ZYA grade, from Ted Pella; single/double layer graphene, grown on 90-nm SiO_2 wafers, from Graphene Supermarket) held at room temperature. In separate experiments, the IL deposition rate was measured as a function of the cell temperature and the evaporation time by a quartz crystal microbalance (Nor-Cal Products) placed below the effusion cell.[5] Consistent results of the film growth rate were also obtained by the RHEED measurements taking into account the grazing penetration of probe electrons in ultrathin IL films and the gradual loss of the diffraction features from HOPG. The deposition of both the cation $[EMIM]^+$ and the anion $[Tf_2N]^-$ was confirmed by monitoring the partial pressures of the parent and/or fragments of the ions using a residual gas analyzer ($m/z \leq 200$).[2, 4] In addition, the infrared spectra of the deposited IL and the liquid inside the crucible after multiple thermal cycles were recorded *ex situ* and confirmed to be the same as that of the original liquid.

RHEED Experiments.

Electron diffraction images of the solid-IL interfacial structures were recorded at grazing incidence angles in a reflection geometry, using an imaging assembly consisting of a phosphor screen and a charge-coupled device (CCD) camera. The acceleration voltage for the electrons in most of our measurements was 30 kV, resulting in a de Broglie wavelength of $\lambda \approx 0.07$ Å. The average flux of electrons was maintained at a low level on the order of <1 pA/mm^2, and no sample damage or modification was observed as a result of long electron exposure. Typically, a diffraction image was acquired in a few seconds. The base pressure in the diffraction chamber was at the level of 10^{-10} mbar, where most of the residual gas species were hydrogen molecules and ions and the water partial pressure was below the detection limit. The specimens were supported on a 5-axis high-resolution manipulator (3 translational and 2 rotational degrees of freedom), which is coupled to a cryostat to enable experiments at temperatures between <20 K and 500 K, using liquid cryogen and an internal heater. In the present study, the sample temperature was directly measured within an accuracy of a degree by a K-type thermocouple attached to the specimen surface, and the heating (cooling) rate was 4.2 (3.0) K/min at ~250 K and 7.0 K/min during desorption of the IL.

The probe depth in RHEED measurements can be estimated by a trigonometric relation considering the elastic mean-free-path length of 30-keV electrons in the IL, which is ~57 nm, and the angle of grazing incidence, which is typically on the order of a degree. For 10-keV electrons, the elastic mean-free-path length in the IL decreases to ~20 nm, so only the topmost layer of the interfacial assembly is probed.

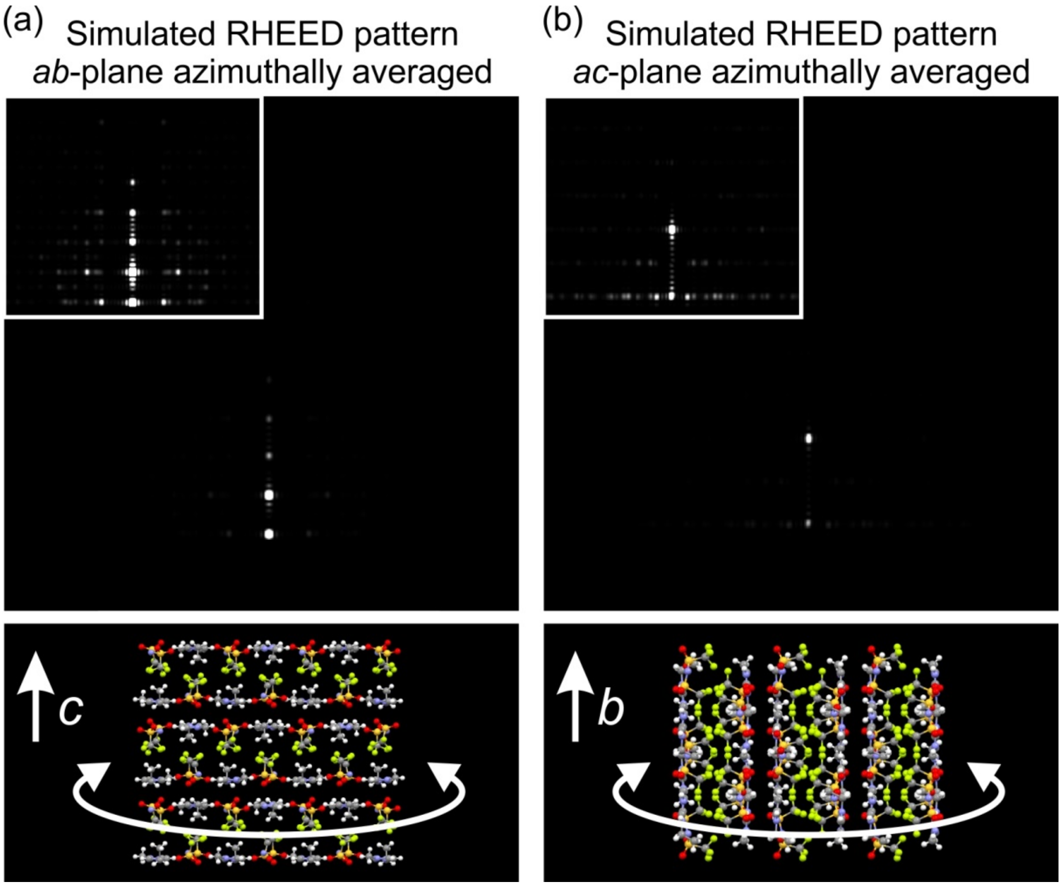

Fig. S1. Simulated RHEED patterns of the crystalline IL structure, with (a) the orthorhombic *c* axis being perpendicular to the surface and the *a*-*b* plane azimuthally rotated and averaged; and (b) the orthorhombic *b* axis being perpendicular to the surface and the *a*-*c* plane azimuthally rotated and averaged. The upper left insets show the intensity-enhanced central region.

References

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