Supporting Information

Two-Step Freezing in Alkane Monolayers on Colloidal Silica Nanoparticles: From a Stretched-Liquid to an Interface-Frozen State

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Experimental Section

Thin films of C_{18} were prepared by self-assembly from *n*-heptane solution (0.03 mol/L) on polished Si (100) wafers (Semiconductor Processing Co., Boston, MA) with dimensions of approximately 10 mm × 10 mm. The wafers have a native silicon-oxide film of about 12-25 Å thickness. The C_{18} films were prepared on these silicon wafers via spin-coating from *n*-heptane solutions (ambient conditions, RT, 3000 rpm). The nonvolatile alkanes remain on the substrate after heptane evaporation with a coverage that scales linearly with the concentration.

The grazing incidence X-ray diffraction (GIXD) measurements of the final film structure were carried out on a Xeuss SAXS/WAXS system (Xenocs SA, France) at T=363 K. A multilayer focused Cu Kα X-ray source (GeniX3D Cu ULD), generated at 50 kV and 0.6 mA, was utilized. The wavelength of the X-ray radiation was 0.15418 nm. A semiconductor detector (Pilatus 300 K, DECTRIS, Swiss) with a resolution of 487×195 pixels (pixel size = 172×172 m^2) was applied to collect the scattering signals. Each GIXD pattern was collected with an exposure time of 600 seconds. The incident beam made an angle of ~ 0.5° with the SiO_2 surface, which is slightly greater than the critical angle for investigated material.

Results and discussion

In diffraction scans with wave vector transfer q_z parallel to the surface normal, three Bragg peaks characteristic of the lamellar ordering of the C_{18} molecules are observed – see Figure S1. By contrast in scans with wave vector transfer q_{xy} perpendicular to the surface normal (see Figure S2) no such layering peaks, but Bragg peaks at larger

q_{xy} typical of the lateral ordering within the C_{18} lamellae were observed. This indicates that the layering direction in the crystallized films are parallel to the silica surface normal, i.e. the C_{18} molecules are oriented with their long axis parallel to the silica surface normal. The peaks at $q_{xy}^{=}$ 1.35, 1.38, 1.63 to 1.72 $Å^{-1}$ can be indexed as the (010), (011), (100) and (111) Bragg reflections of a triclinic unit cell.

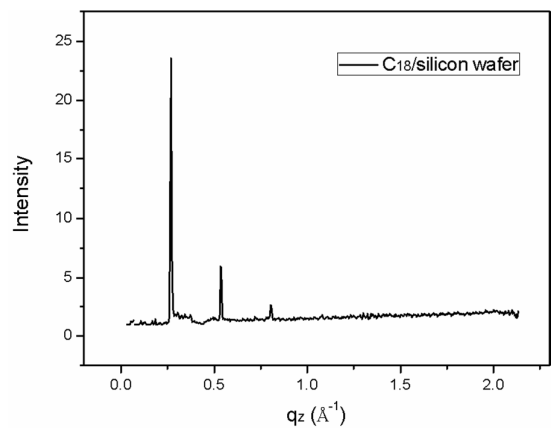

Figure S1: X-ray intensity scattered from a thin film of C_{18} on a silica substrate with wave vector transfer q_z parallel to the silica surface normal.

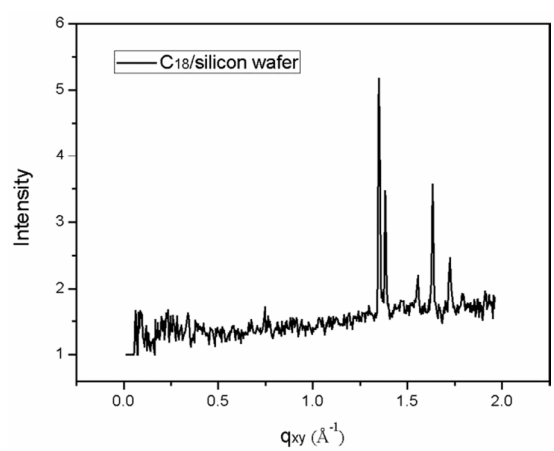

Figure S2: X-ray intensity scattered from a thin film of C_{18} on a silica substrate with wave vector transfer q_{xy} parallel to the substrate surface.