Polymer Pen Lithography with Lipids for Large-Area Gradient Patterns

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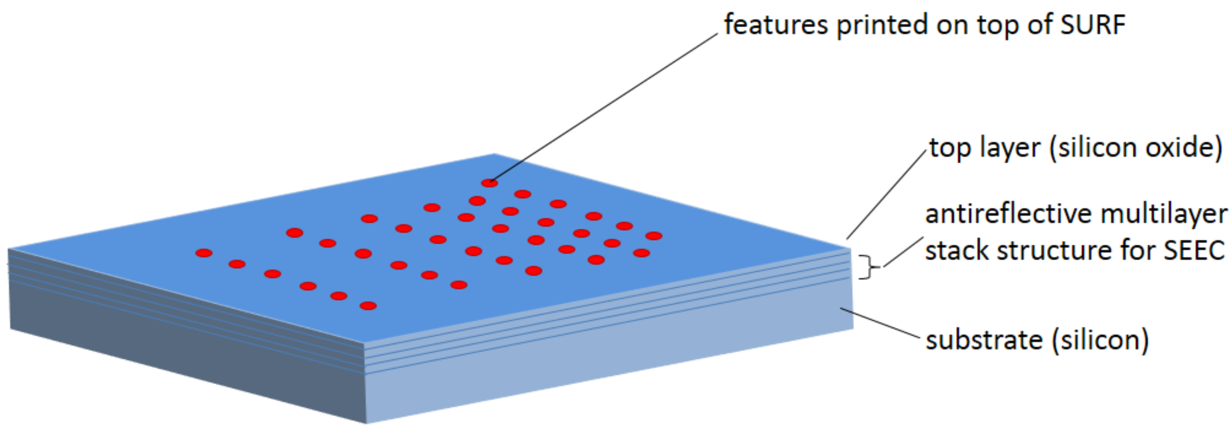

Figure S1. Schematic of the commercial SiO2 SURF substrate. Adapted from Supporting Information in previous publication[1] and the Nanolane product website.[2]

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[1] Hirtz, M., Corso, R., Sekula-Neuner, S. & Fuchs, H. Comparative Height Measurements of Dip-Pen Nanolithography-Produced Lipid Membrane Stacks with Atomic Force, Fluorescence, and Surface Enhanced Ellipsometric Contrast Microscopy. *Langmuir* **27,** 11605–11608 (2011).

[2] http://www.nano-lane.com/seec-technology/visualization/

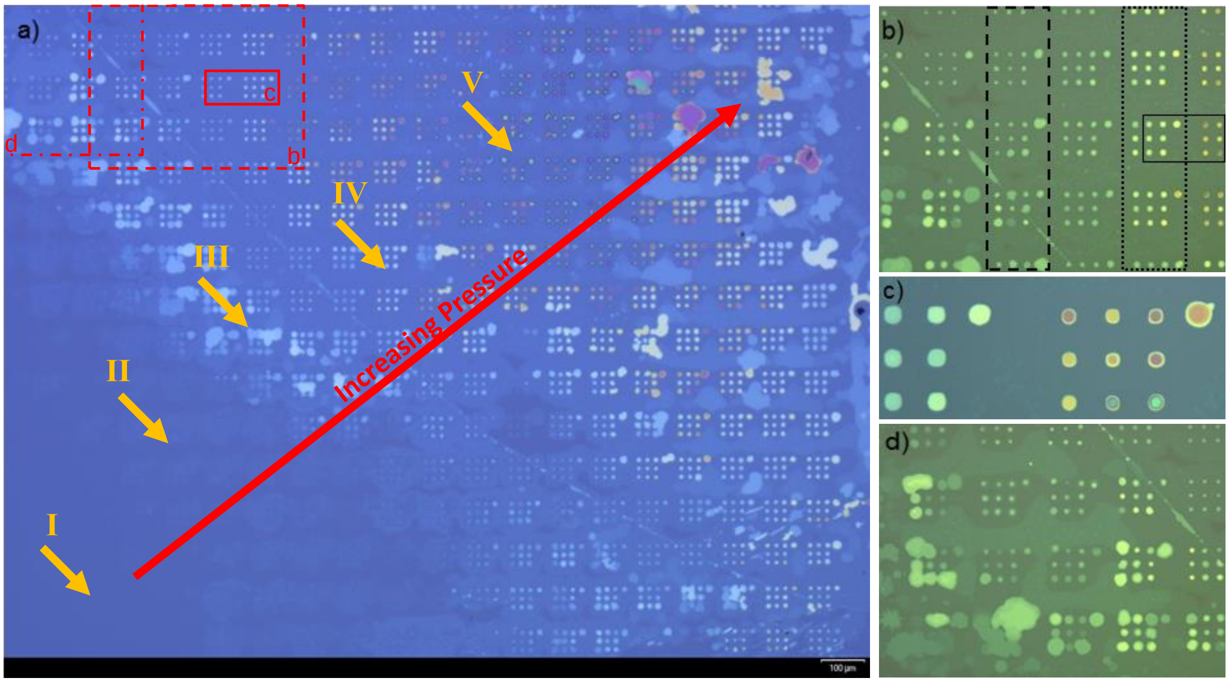

Figure S2. SEEC microscopy image of a steep pressure gradient sample. (a) Overview image of the sample produced with an ink-overloaded stamp and extensive pressure on the upper right corner. (I) area of no transfer, stamp was not in contact with substrate. (II) Lowest pressure region, features spread out into a base layer. As there is excessive amount of ink, the single dot features from one pen already merge, but features from neighboring pens are still distinct. (III) Region of intermediate pressure, the base layer of some neighboring pen's features already merge, but not all. Features are comparably irregular, due to the uneven inking in the overloaded stamp. (IV) High-pressure region, where the base layer is now forming a confluent hydrophobic background. Features on top are well defined, droplet shapes. (V) Start of the area with excessive pressure. Here, more defects and even inverse structures (membrane stacks higher than the dot features in between the features written by neighboring pens) are observed due to shielding effects of the pyramidal pens. The scale bar equals 100µm. (b) Close-up of the area marked b in (a) showing clear and well defined features. (c) Higher magnification of the area marked as c in (a) and by solid box in (b) showing well defined features shape at high pressure stamping. (d) Close-up of the area marked d in (a) showing an intermediate-pressure region with inhomogeneous features shape due to irregular transfer by the ink-overloaded stamp.

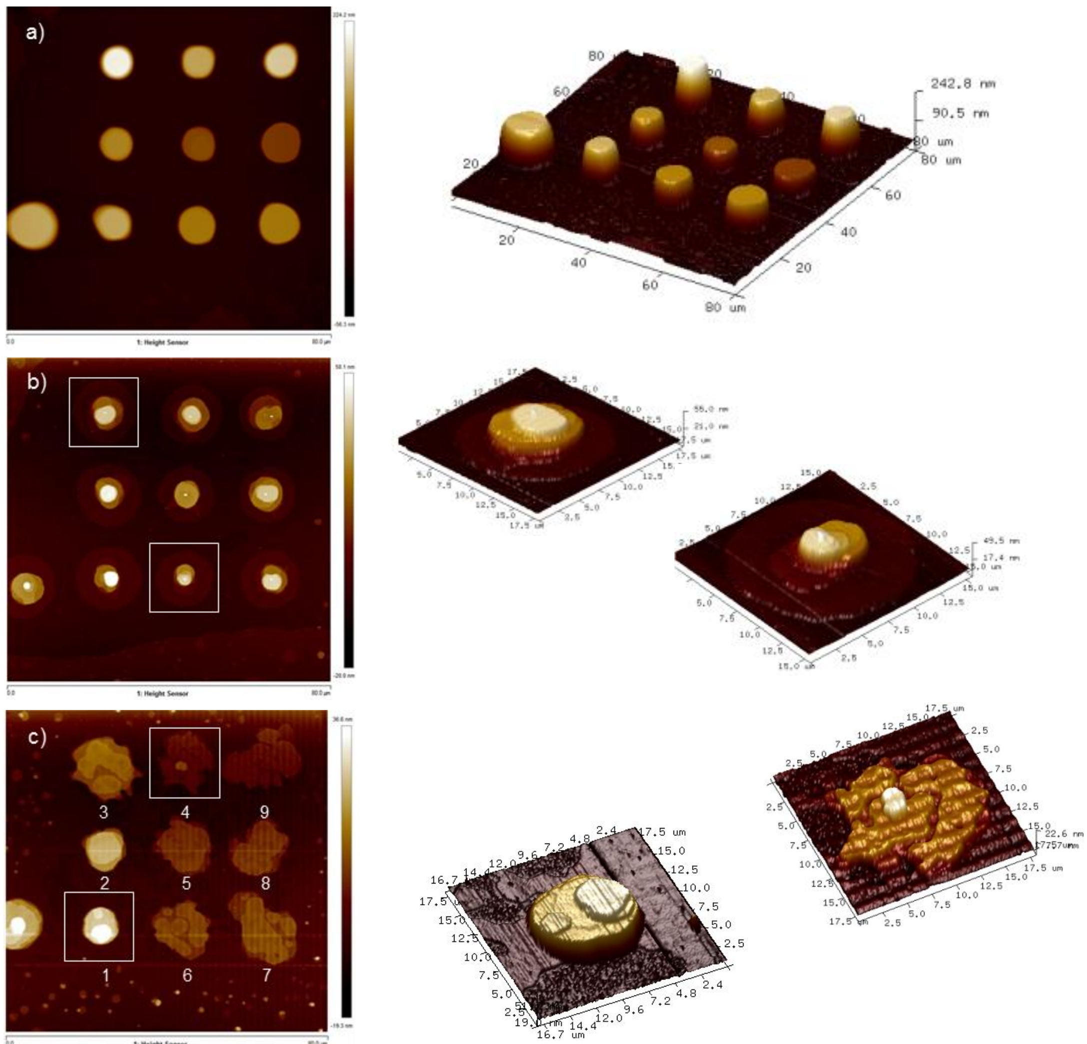

Figure S3. AFM microscopy images of selected features of the sample shown in Figure S1. (a) The high-pressure region shows flattened droplet features with relative uniformity in shape and area (77.64 ± 9.55 μm^2) and much higher features (138.19 ± 34.91 nm) in comparison to the flat, few-layer membranes observed on samples without confluent base layer. (b) Shows features in the medium pressure region, features start losing uniform droplet shape and developing a more flat, membrane stack structure. (c) In the low-pressure regions, without the confluent hydrophobic base monolayer of lipids, features display flat membrane structures, similar to the patterns obtained by the stamps inked with spincoating. The numbers indicate the order in which the dots were stamped. Due to the massive inkload on the stamp, one can clearly notice depletion effects: more ink in the first features, as there is not enough time during stamping for ink-reflow from the pen base to the pen apex, an effect similar to what is observed in highly lipid-loaded DPN tips.[3]

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[3] Förste, A.; Pfirrmann, M.; Sachs, J.; Gröger, R.; Walheim, S.; Brinkmann, F.; Hirtz, M.; Fuchs, H.; Schimmel, T. Ultra-Large Scale AFM of Lipid Droplet Arrays: Investigating the Ink Transfer Volume in Dip Pen Nanolithography. *Nanotechnology* **2015**, *26*, 175303.

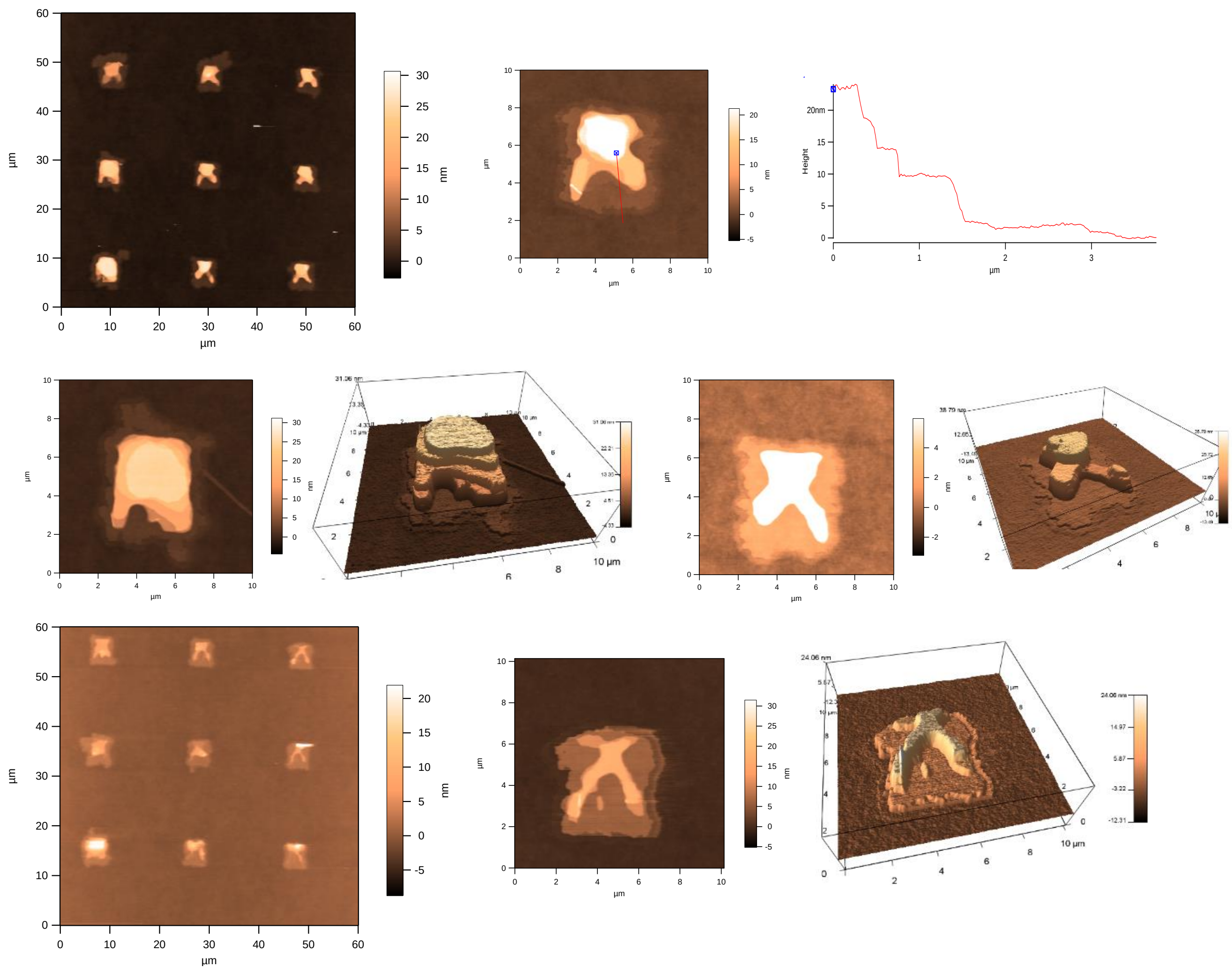

Figure S4. Examples of x-shaped features printed at higher-pressure regions with spincoated inked stamps on glass. The main base structure remains square like as expected from the μCP like transfer at higher pressures, but edge effects lead to formation of the x-shaped features on top during pen retraction. Likely, the four edges of the pyramidal pens reemerging upon pen retraction act as singular sources of pronounced ink transfer, therefore leading to the x-shaped feature by "writing" from the corners of the base square to merging in the center when the pen apex loses contact with the substrate.