An Ink Transport Model for Prediction of Feature Size in Dip Pen Nanolithography

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Section S1: Selecting the range of values for meniscus height and surface ink diffusivity

A range of values was used for the meniscus height because accurate models that predict the meniscus geometry are not available from literature. Direct visualizations of the water meniscus have shown that the meniscus is at least 10–100 times larger than the predictions of Kelvin's equation for capillary condensation or molecular dynamics simulations.[S1] Therefore, a range based upon observations, 2–10 nm, was selected for the meniscus height. This is based upon the typical thickness of the water film observed on the gold surface during AFM in the ambient.[S2,S3]

The value of surface diffusivity (D_s) for MHA ink cannot be obtained from the literature. The physical quantity reported as 'diffusion coefficient' (D) in DPN literature is not representative of 'diffusivity' as defined by Fick's first law of diffusion. Instead, the reported D values quantify the area coverage rate observed during DPN writing. The area coverage rate for our experiments (given by: Vw) is 0.011–0.015 μm^2/s, and is close to the reported D values of 0.015–0.085 μm^2/s. A lower limit estimate of D_s can be made from the surface diffusivity of octadecanethiol (ODT) ink which was obtained using molecular dynamics simulations as: 4.15–5.26 x10^{-9} m^2/s.[S4] As it is known that MHA is a 'faster' ink than ODT, the range for MHA surface diffusivity was selected as 5–25 x10^{-9} m^2/s.

Section S2: Empirical estimation of cut-off velocity from LFM scans

We have used the Lateral Force Microscopy (LFM) scan data to empirically estimate the cut-off velocity. Cut-off velocity identifies the writing speed at the transition from writing of continuous lines to discontinuous lines. For large differences in writing speeds, visual inspection of the LFM scan data was used as a first pass check of cut-off velocity. As shown in Figure S1, the cut-off can be reliably bounded within the 0.25 μm/s – 1 μm/s range via visual inspection. This is supported by the lengthwise force profiles of the lines.

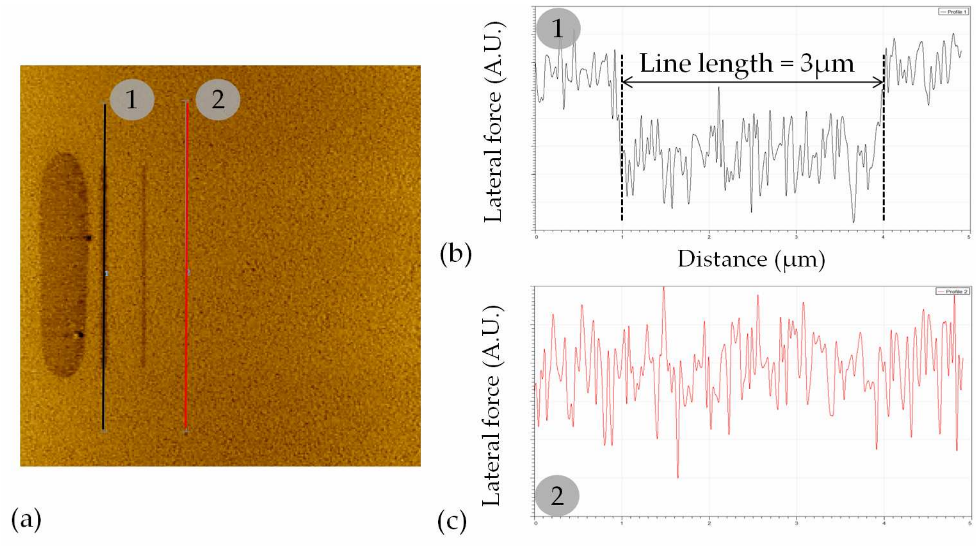

Figure S1. Use of lengthwise lateral force profiles to distinguish continuous and discontinuous lines written in the writing speed range of 0.01–5 µm/s. (a) Lateral force microscopy scan. (b) Force profile of a continuous line. (c) Force profile of a discontinuous line or line with no writing.

However, visual inspection may be subjective at writing speeds close to the cut-off. Therefore, at such writing speeds we have used the force profile along the length of the line to identify the continuous lines. This technique reduces the subjectivity involved in distinguishing between the continuous and the discontinuous lines. Lines of the same length (3 µm) were written at various writing speeds in the range of 0.25 µm/s – 1 µm/s. LFM scan and force profiles of the lines written within this range are shown in Figure S2. For continuous lines, one can verify the 3 µm length as the distance over which the lateral force is significantly different from the force on the bare substrate surface. However, no significant difference in force is observed along the length of the discontinuous lines. We can identify such lines as being discontinuous, as opposed to being the bare surface, via a visual inspection of the LFM scan in which the outline of the line is visible.

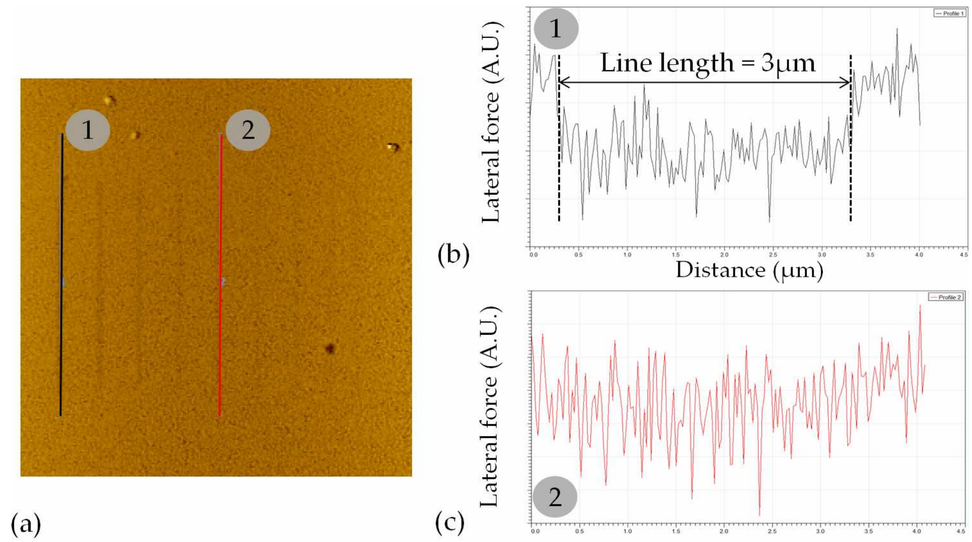

Figure S2. Use of lengthwise lateral force profiles to distinguish continuous and discontinuous lines written in the writing speed range of 0.25–1 μm/s. (a) Lateral force microscopy scan. (b) Force profile of a continuous line. (c) Force profile of a discontinuous line.

Section S3: Estimation procedure for ink solubility parameter α

The attempt frequency of ink detachment, v, is not known accurately, therefore experimental data was used to obtain an estimate for α. Two short lines were written at identical speeds, one before and the other after writing a long-wide line with the same tip. The loss in the amount of ink on the tip, ΔN, due to writing of the long line was calculated from the surface area of the line. Neglecting the first term in eq 13, the width of the short lines is related to the amount of ink on the tip by: $N\alpha \sim b\rho Vw$. The width of the second short line is less than the width of the first line due to a decrease in N. Thus, α is obtained from the change in width of the two short lines, Δw, and the change in N as: $\alpha \sim \rho bV\Delta w/\Delta N$.

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