Picogram material dosing of microstructures

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A solution delivery platform comprised of a suspended microcapillary connected to a microwell enables picogram solute deposition on suspended structures. Precision material placement in the capillary from a 100 pl drop inkjetted into the well is achieved without the destruction of the microstructure and adjacent submicron electrostatic gaps. This method scales to smaller structures without the need for drop miniaturization. The theory behind the solute transfer in the system is developed. Three regions in the drying process are observed and match with the model. The “accumulation” region builds solute concentration in the capillary. The “solidification” region initiates the solidification of solute starting at the free end of the capillary. The “termination” region is characterized by a rapid increase in the solidification due to an increase in the well concentration near the end of the drop lifetime. The accumulation time and solidification rate dependence on concentration compare well with the model. © 2009 American Institute of Physics.

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I. INTRODUCTION

Maskless fabrication techniques have several advantages over conventional photolithographic techniques for fabrication on the micro- and nanoscales. These advantages include rapid prototypes where the need for a new mask for each design iteration is eliminated. Direct deposition is an additive process and, therefore, costly materials can be conserved. Elevated processing temperatures causing substrate distortion due to temperature coefficients of expansion mismatch can be eliminated with maskless deposition.¹ Deposition onto released cantilever structures with micron and submicron scale dimensions may only be realized with maskless techniques since photoresist deposition would lead to the destruction of the device.^{2,3} Also, implementation of chemical sensor arrays, which require multimaterial deposition onto single chip surfaces, would require multiple mask steps, whereas maskless techniques such as ink-jet printing and microcapillary deposition are less costly.^{2,4}

Direct material deposition and manipulation on these scales have been achieved through techniques such as atomic force microscopy (AFM), “dip pen” lithography and inkjet printing.⁵ Although AFM and dip pen lithography techniques provide precise deposition on the nanoscale, both require high precision three-dimensional control of the fabrication unit and are considered slow processes.¹ Inkjet printing technology is a more rapid deposition technique. However, direct inkjet printing results in lower resolution features, where the state-of-the-art spot size is a few microns in diameter.^{1,6} Nonuniform structures may result from “coffee ring” formation⁷ and low viscosity fluids and inks are necessary for repeatable deposition. Direct inkjet deposition necessitates large dimensions⁴ leading to, in the case of mass sensitive concentration sensors, poor mass concentration reso-

lution detectors.⁸ A more ideal deposition method would provide uniform deposition confined to only the microstructure. Miniaturizing the inkjet drop size, which proves more difficult for repeatable deposition due to issues such as jet clogging, is not necessary for micron and nanoscale material placement using the current method.

An alternative approach explored in this paper is to deposit drops into a well and have the solution wick into an adjacent suspended capillary. An example system of a capillary created on a cantilever is illustrated in Figs. 1(a)–1(c). This fabrication method alleviates some of the major problems with inkjetting and allows for picogram dosing, precise material placement with microscale resolution, and uniform deposition which is not plagued by the coffee ring phenomenon. Alignment of the deposition tool is set by the more relaxed requirement to hit the well. If the inkjet drop placement is misaligned by tens of microns, there is not a direct translation of misalignment to the deposited material, as is the case for other maskless deposition techniques such as dip pen and “fountain pen” nanolithographies.

The capillary is designed along the length of the structure to be dosed with material. We have previously shown a qualitative proof of concept utilizing this method where micron-scaled grooves and slots have been dosed with precise material amounts of 100 pg per drop resolution.^{2,3} These scaled microelectromechanical system (MEMS) structures were dosed with a receptor polymer and used as a microcantilever gas vapor detector with femtogram mass resolution in air. The fabrication method demonstrated a repeatable deposition technique on sensor arrays preserving the integrity of the structure constituted by micron-scaled mechanical beam widths and submicron electrostatic gaps. Figure 1(b) shows a representative microgroove capillary device dosed with this method. The material is precisely placed in the 2 μm wide, 120 μm long suspended capillary without destruction of the

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FIG. 1. (Color online) (a) Illustration of the well and capillary system where the well serves as a target for the drop. (b) Digital image (top view) of the fabricated well and capillary system after three drops of polythiophene in trichlorobenzene solution. (c) Cross section of a filled well and capillary during the drying process. The solute extent grows from the end of the channel back toward the entrance to the well. (d) A focused ion beam cross section at the tip of the $120 \mu\text{m}$ long suspended micro-groove structure is shown after solvent drying. The cross section in (d) also illustrates the dried material in the micro-groove.

structure or the $0.6 \mu\text{m}$ wide electrostatic gaps. A focused ion beam cross section of a microgroove capillary is shown in Fig. 1(d).

In the current work, the theory of material transfer in the well and capillary system is presented. Simulation and experimental verification show excellent agreement of the model of this precise dosing process.

II. THEORY

The complex well and capillary system cross section is shown in Fig. 1(c). The well is sized to accommodate the volume of the inkjet drops. The capillary runs the length, L_c , of the MEMS structure [Fig. 1(c)]. Qualitative inspection of the MEMS microcapillaries after solution deposition shows nearly 100% solute transfer to the capillary with little to no material left in the well at the base of the capillary. The model explaining this phenomenon is derived by extending a prior model describing coffee ring formation in a drying drop on a surface.⁷ Once solution is deposited into the well, as shown in the digital image in Fig. 1(b), surface tension drives the solution into the capillary. The solution-solid transition location, L_T , begins from the end of the capillary, $x = L_c$, and recedes back toward the entrance of the well. Therefore, the polymer extent grows from the end of the channel. This is illustrated in Fig. 1(c). The solute transfer theory assumes a capillary fully loaded with solution. The speed of the capillary filling process due to surface tension is

much larger compared to the drying process for low vapor pressure solvents such as toluene and trichlorobenzene.

The solvent mass rate of change in an infinitesimal element, dx , in Fig. 1(c) is

$$\rho \frac{\partial h_c}{\partial t} dx \times w_c = \rho w_c h_c v(x, t) - \rho w_c h_c v(x + dx, t) - J_s w_c dx, \quad (1)$$

where ρ is the solvent density, h_c is the capillary height, w_c is the capillary width, and J_s is the evaporation rate of the solvent in units of $(\text{kg}/\text{m}^2/\text{s})$. The one-dimensional velocity profile is described by $v(x, t)$ and is a function of time, t , and space, x , where the origin, $x=0$, is located at the entrance from the well into the capillary. The first term in Eq. (1) on the right hand side is the solvent mass flowing into dx , the second term is the solvent mass flowing out of dx , and the final term describes the solvent mass loss to due to evaporation at the liquid-air interfaces in the capillary. Equation (1) assumes a microgroove capillary shape, as shown in Fig. 1(d).

Equation (1) reduces to

$$\frac{\partial}{\partial x} v(x, t) = - \frac{1}{h_c} \left(\frac{J_s}{\rho} + \frac{\partial h_c}{\partial t} \right). \quad (2)$$

In steady state after the initial fill, the time rate of change of the capillary height is

$$\frac{\partial h_c}{\partial t} = 0. \quad (3)$$

This is a valid assumption for short capillary microchannels, where the solution volume fill rate at the capillary base can accommodate the volume evaporation rate of the solvent off of the surface of the liquid in the capillary. In Eq. (2), J_s is assumed to be constant for a dilute solution. However, once the concentration reaches a critical concentration, c_r , the solute originally suspended in solution becomes a semisolid material with solvent diffusing out to the evaporation interface. A concentration dependent evaporation and, thus, velocity gradient describes this transition region. A Fermi function is chosen in the model to describe the decrease in evaporation rate when the solution becomes very concentrated with the solvent diffusing out of the solute. The choice of the Fermi function provides a convenient analytic way to model the behavior as the material transitions from liquid to solid phase. With this addition, Eq. (2) becomes

$$\frac{\partial}{\partial x} v(x, t) = - \frac{J_s}{\rho h_c} \times \frac{1}{1 + \exp \left[\frac{(c(x, t) - c_r)}{\mu} \right]}, \quad (4)$$

where $c(x, t)$ is the concentration profile along the length of the capillary and μ is a transition coefficient.

The evaporative flux in the meniscus region is dependent on interfacial temperature and pressure jumps⁹ and is modeled by

$$J_s = a(T_{lv} - T_v) + b(P_l - P_v), \quad (5)$$

where T_{lv} is the liquid vapor interface temperature, T_v is the vapor temperature, P_l is the liquid pressure, and P_v is the

vapor phase pressure. The coefficients, a and b , are dependent on the evaporating liquid. The pressure jump, $P_l - P_v$, in the meniscus region is described by the augmented Young–Laplace equation:^{10,11}

$$P_l - P_v = \sigma K - \frac{\bar{A}}{\delta^3}, \quad (6)$$

where σ is the liquid surface tension (N/m), K is the curvature (m^{-1}), $\bar{A}$ is the disjoining pressure constant (J), and δ is the liquid thickness. The first and second terms on the right-hand side of Eq. (6) are described by the capillary pressure and disjoining pressure, respectively. The disjoint pressure is dominant in the extended meniscus region and falls rapidly in the intrinsic meniscus region. A more complex treatment of the pressure difference due to the different meniscus regions in a rectangular microgroove may be found in prior work.¹⁰ Assuming a constant system temperature and a high aspect ratio groove, Eq. (6) is substituted into Eq. (5) yielding

$$J_s = b \left(\sigma \frac{2 \cos \theta_c}{w_c} - \frac{\bar{A}}{\delta^3} \right), \quad (7)$$

where θ_c is the liquid solid contact angle. Substituting for J_s in Eq. (4) provides

$$\frac{\partial}{\partial x} \nu(x, t) = -B \times \frac{1}{1 + \exp \left[\frac{(c(x, t) - c_r)}{\mu} \right]}, \quad (8)$$

$$B = b \left(\sigma \frac{2 \cos \theta_c}{w_c} - \frac{\bar{A}}{\delta^3} \right) \times \frac{1}{\rho h_c}. \quad (9)$$

The solute rate of change in the volume dx is

$$\begin{aligned} h_c w_c \frac{\partial}{\partial t} (c(x, t) dx) &= (h_c w_c) c(x, t) \nu(x, t) - (h_c w_c) c(x \\ &+ dx, t) \nu(x + dx, t) + w_c h_c D \frac{\partial}{\partial x} c(x \\ &+ dx, t) - w_c h_c D \frac{\partial}{\partial x} c(x, t), \end{aligned} \quad (10)$$

where D is the diffusion coefficient of the solute in the solvent. The first and second terms on the right-hand side describe the flow of solute into and out of the infinitesimal element, dx , respectively. The third and fourth terms on the right-hand side describe the diffusion of solute into and out of dx , respectively. A Fermi function is also chosen to describe the diffusion coefficient as a function of concentration:

$$D(x, t) = \frac{D_o - D_\infty}{1 + \exp \left[\frac{(c(x, t) - c_r)}{\mu_D} \right]} + D_\infty, \quad (11)$$

where D_o is the nominal value of solute diffusion in a dilute solution, μ_D is the transition coefficient for diffusion, and D_∞ is a nonzero diffusion value as the concentration of the solution approaches infinity.

III. NUMERICAL ANALYSIS

The nondimensional quantities

$$x^* = \frac{x}{L_c} \quad (12a)$$

$$t^* = B \times t \quad (12b)$$

$$c^*(x^*, t^*) = \frac{c(x^*, t^*)}{c_r} \quad (12c)$$

$$\nu^*(x^*, t^*) = \frac{\nu(x^*, t^*)}{BL_c} \quad (12d)$$

are substituted in Eqs. (4) and (10) to form the normalized coupled partial differential equations

$$\frac{\partial}{\partial x^*} \nu^*(x^*, t^*) = \frac{-1}{1 + \exp \left[\frac{c_r}{\mu} (c^*(x^*, t^*) - 1) \right]}, \quad (13)$$

$$\begin{aligned} \frac{\partial}{\partial t^*} c^*(x^*, t^*) &= - \frac{\partial}{\partial x^*} [c^*(x^*, t^*) \times \nu^*(x^*, t^*)] + \frac{D^*(x^*, t^*)}{BL_c^2} \\ &\times \frac{\partial^2}{\partial x^{*2}} c^*(x^*, t^*), \end{aligned} \quad (14)$$

where

$$D^*(x^*, t^*) = \frac{D_o - D_\infty}{1 + \exp \left[\left(\frac{c_r}{\mu_D} \right) (c^*(x^*, t^*) - 1) \right]} + D_\infty. \quad (15)$$

The nondimensional initial velocity and concentration are

$$\nu^*(x^*, 0) = 0, \quad (16a)$$

$$c^*(x^*, 0) = \frac{c_o}{c_r}. \quad (16b)$$

The spatial derivative of the velocity at the inlet from the well is

$$\frac{\partial}{\partial x^*} \nu^*(0, t^*) = \frac{-1}{1 + \exp \left[\frac{c_r}{\mu} (c^*(0, t^*) - 1) \right]}, \quad (17)$$

and the concentration at the inlet from the well is

$$c^*\{0, t^*\} = \frac{1}{c_r} \times \frac{c_o V_{\text{drops}}}{V_{\text{drops}} - \frac{\beta}{B} t^*} \quad (18)$$

where c_o is the initial solute concentration in the well, V_{drops} is the initial volume of solution inkjetted into the well, and β is the effective volume evaporation rate (m^3/s) of the solvent in the well. This evaporation in the well is a diffusion limited process.^{12,13} The solvent velocity and the flux of solute at the end of the cantilever are zero:

$$\nu^*(1, t^*) = 0, \quad (19a)$$

FIG. 2. (Color online) FEA of the normalized concentration profile, $c^*(x^*, t^*) = c(x^*, t^*)/c_r$ vs the normalized distance, x^*/L_c , along the capillary. At the end of the capillary, the concentration increases at a higher rate. Toward the end of the lifetime of the drop, the rapid concentration growth at the well affects a rapid change in the growth in the capillary.

$$\frac{\partial}{\partial x^*} c^*(1, t^*) = 0. \quad (19b)$$

Figure 2 shows the finite element analysis (FEA) using a one-dimensional (1D) solver in COMSOL MULTIPHYSICS (Burlington, MA) concentration profile at different times, t^* , for a polythiophene in trichlorobenzene solution using the properties: $L_c = 120 \mu\text{m}$, $h_c = 3.2 \mu\text{m}$, $w_c = 2 \mu\text{m}$, $\rho = 1454 \text{ kg/m}^3$, $V_{\text{drops}} = 1.08 \times 10^{-13} \text{ m}^3$, $J_s = 0.01 \text{ kg/m}^2/\text{s}$, $\beta = 1.47 \times 10^{-15} \text{ m}^3/\text{s}$ (effective volume evaporation was experimentally verified), $D_o = 1.57 \times 10^{-10} \text{ m}^2/\text{s}$, $\mu = 50$, $\mu_D = 50$, $D_\infty = 2 \times 10^{-13} \text{ m}^2/\text{s}$, and $c_r = 800 \text{ kg/m}^3$. For this case, $B = 2.15 \text{ s}^{-1}$. The diffusion coefficient values are extracted from that measured in the literature.^{14–16} Estimated values were used for μ , μ_D , and c_r . The evaporation rate, J_s , was the lone fitting parameter adjusted to fit the numerical simulation to the empirical time-lapse data discussed in Sec. IV. The fitted value of J_s , while 100 times larger than the evaporation rate in the intrinsic meniscus region, appears reasonable because evaporation in the very thin film is dominated by the disjoining pressure jump described in Eq. (6). The concentration at the capillary end, $x = L_c$, grows rapidly. In the FEA, once the critical concentration, c_r , is reached the solution system is considered a solid and the velocity is zero. The concentration grows rapidly near the solution-solid transition location, L_T . Toward the end of the lifetime of the inkjetted drops, $t^* = 156$ in Fig. 2, there is a rapid increase in the solution concentration in the well. This causes a rapid increase in the rate at which the solidification front, L_T , recedes back towards the well opening.

IV. EXPERIMENTS

The suspended microcapillaries were fabricated in the SiGe 0.35 μm BiCMOS (complementary metal-oxide semiconductor) technology from Jazz Semiconductor (Newport Beach, CA) followed by post-CMOS micro-machining.¹⁷ After foundry CMOS fabrication, three dry etch steps were used for definition and release of the MEMS structures and were followed by inkjet deposition into the well.²

The width and height of the structure containing the capillary are 4 and 4.9 μm , respectively. Polythiophene was dissolved in a trichlorobenzene solvent and deposited into the wells. This polymer was chosen for the experiments since it

FIG. 3. (Color online) Digital images during the drying process after three 5 kg/m^3 solution drops. An arrow in each image indicates the solution-solid transition location, L_T . At time, $t = 80 \text{ s}$, the channel is completely filled with polymer.

is opaque. This allows tracking of the drying process using digital video images. Trichlorobenzene is chosen for its low vapor pressure and evaporation rate. Solvents with higher vapor pressures evaporate too fast to track the evaporation process with the current experimental setup. The molecular weight of the polythiophene is 11 570 g/mol and its estimated diffusion coefficient in a dilute solution is $1.57 \times 10^{-10} \text{ m}^2/\text{s}$ (extracted from prior reported data¹⁶).

For each of the structures, three solution drops were inkjet deposited into the wells, corresponding to approximately 100 pL of solution. Video images of the drying process were taken at 10 frames/s. Figure 3 shows optical photos as the solution was drying for $c_o = 5 \text{ kg/m}^3$. An arrow in each frame indicates the transition between the “light” and “dark” portions of the channel. The light region is assumed to be the portion of the capillary with solution and the dark region is assumed to be dried solute, as illustrated in Fig. 1(c). Software was written to track the transition between the light and dark portions in the channel for each frame. The tracking software resolution, limited by the resolution of the imaging apparatus, is 2 μm . The transition location, L_T , was measured over several experiments under different initial concentrations: 0.5, 1, 2.5, 5, and 7.5 kg/m^3 .

The normalized transition location, L_T/L_c , versus time is shown in Fig. 4 for the different inkjet solution concentrations. The experiment was repeated twice for the 0.5, 2.5, 5, and 7.5 kg/m^3 concentrations. The measured data are compared to the FEA model. A small dark region was observed at distances close to, but in front of, the solidification front, L_T . This region, which is referred to as the “1st front” in Fig. 4, merges with the solidification front, “2nd front,” at later times during the drying process. The region is observed at

FIG. 4. (Color online) The solidification front is tracked during the drop drying process and is compared to FEA. The profile is measured and shown for the different initial solution concentrations: $c_o = 0.5 \text{ kg/m}^3$ in (a), $c_o = 1.0 \text{ kg/m}^3$ in (b), $c_o = 2.5 \text{ kg/m}^3$ in (c), $c_o = 5 \text{ kg/m}^3$ in (d), and $c_o = 7.5 \text{ kg/m}^3$ in (e). The accumulation and solidification regions are both visible [(a)–(c)]. The rapid increase in the rate L_T that moves back toward the entrance of the well occurs when the concentration in the well begins to grow rapidly at the end of the drop lifetime.

times approximately equal to 64, 63, 69, and 65 s for the 1, 2.5, 5, and 7.5 kg/m^3 , respectively. Two fronts were not experimentally observed for $c_o = 0.5 \text{ kg/m}^3$. This “two front” behavior is not predicted by the model; however, the true solidification front, L_T , is hypothesized to be a region between the two fronts. There was difficulty for the tracking software to resolve the two fronts since the width of the first front was slightly larger than the resolution of the imaging apparatus, thus making it difficult to fully capture the merge of the two regions. A higher resolution imaging apparatus would be needed to further quantify this merge behavior.

There are three regions in time to note in the experiments and model shown in Fig. 4(b): an initial “accumulation region” where the solid solute has not yet begun to form at the end of the channel, a “solidification region” where the transition location decreases with time and a “termination region” where the rapid increase in the well concentration causes a large increase in the solidification rate. The accumulation time and the solidification rate are dependent on the initial drop concentration. The accumulation region is apparent in the model and the experimental data for the lower solution concentrations, $c_o \leq 5 \text{ kg/m}^3$. For the higher solution concentration, $c_o = 7.5 \text{ kg/m}^3$, the accumulation region is too fast to observe in the experiments. This is due to the finite amount of time ($\sim 9 \text{ s}$) between the deposition of the drops and the time the digital camera begins to acquire images of the drying process. The accumulation dependence on the initial concentration is evident; lower initial solution concentrations result in longer accumulation times. The measured accumulation times in the experiments for the varying initial concentrations are shown in Fig. 5(a) and compared to the FEA expected accumulation times. The theory and experiments compare to within 27%.

The solidification region and the rate at which the transition front moves are also concentration dependent. The solidification rates, $|dL_T/dt|$, are extracted from both the FEA model and experiments at times shortly after the accumulation region ends for the $c_o \leq 5 \text{ kg/m}^3$. The initial drying rates are extracted for $c_o = 7.5 \text{ kg/m}^3$. The experimental rates are plotted as a function of initial solution concentration in Fig. 5(b). The FEA and second front experimental data match to within 13% for all but the lowest concentration tested.

The rate at which L_T moves at times near the end of the drop lifetime increases due to the rapid increase in the well concentration. These effects are evident in the experimental and FEA profiles for the initial concentrations of $c_o = 0.5 \text{ kg/m}^3$ in Fig. 4(a), $c_o = 1 \text{ kg/m}^3$ in Fig. 4(b), and $c_o = 2.5 \text{ kg/m}^3$ in Fig. 4(c). The trends of the rate increase match very well with the model cases.

Capillary structures with varying groove aspect ratios and $200 \mu\text{m}$ lengths were fabricated. Three drops of 5 kg/m^3 of polythiophene in trichlorobenzene were deposited in the wells of each of the structures. The fill rate versus channel width of grooves with two channel heights were measured and compared to the FEA results. Figures 6(a) and 6(b) show the fill rate versus width for the $h_c = 3.2 \mu\text{m}$ and $h_c = 1.6 \mu\text{m}$ channels, respectively. The advancement of the liquid front due to capillary action stopped short of the $200 \mu\text{m}$ channel length for two cases: (1) $h_c = 1.6 \mu\text{m}$, w_c

FIG. 5. (Color online) (a) The accumulation times are extracted from the experiments at different initial solution concentrations and are compared to the model. The data for both observed fronts are shown. (b) The solidification rates at times shortly after the end of the accumulation region are also compared with the model at varying initial concentrations.

$=4.5 \mu\text{m}$ and (2) $h_c=1.6 \mu\text{m}$, $w_c=5 \mu\text{m}$. The liquid front was pinned for the two cases at 177 and 70 μm from the well entrance, respectively. The FEA results in Fig. 6(b) reflect these pinned liquid lengths. The channel aspect ratio affects the liquid meniscus shape in the capillary and has a large effect on the drying process and the solidification rate. A normalization formula for the evaporation rate,

$$J_s = 0.01 \frac{\text{kg}}{\text{m}^2 \text{s}} \times \frac{2 \times 10^{-6} \text{ m}}{w_c}, \quad (20)$$

was used to generate the FEA in Fig. 6. The capillary height for the FEA data is assumed to be the structure height of the capillary groove. This assumption is not valid for larger capillary widths. The effective height of the liquid in the capillary depends on the shape of the meniscus which is reduced at wider channel widths. The meniscus shape and the contact angle, θ_c , would need to be properly evaluated to determine the effective height. A measurement setup to monitor the profile of the meniscus and the contact angle in the different aspect ratio grooves would be needed since the contact angle of the liquid with the groove side walls are not known. As seen from Eq. (7), the effective evaporation per unit surface area, J_s , also has a complex dependence on w_c , θ_c and δ . Although a more sophisticated analytical treatment of the evaporation of a complex meniscus is needed in order to accurately predict the effective J_s and h_c , the measured data show an aspect ratio dependence of evaporation rate where an effective J_s is observed to be inversely dependent on w_c which is also predicted in prior models on evaporation in a

FIG. 6. (Color online) The solidification rate magnitude, $|dL_T/dt|$, vs the channel width for the 3.2 μm (a) and 1.6 μm tall (b) channels. The initial concentration is 5 kg/m³. The measured and FEA rates are shown.

complex meniscus.¹⁰ There is a minimum in the FEA data in Fig. 6(a). The increase in the solidification rate for $w_c > 8 \mu\text{m}$ is due to the accumulation region being too close in time to the termination region. In other words, the solidification begins at times where the drops in the well are close to depletion.

V. CONCLUSIONS

Inkjet printing is an important nonlithographic method which allows for multiple material deposition with precise placement on microstructures for applications including arrayed sensors. Prior work has miniaturized the inkjetted drop in order to achieve higher resolution dosing. This work, in contrast, demonstrates a method to make inkjet printing compatible with suspended structures that can be scaled in size and with adjacent narrow air gaps. The use of a well at the base of the suspended structures provides a target for “large” inkjet drops where the deposited liquid is contained by the target well. Picogram dosing of microslot and microgroove structures were demonstrated without destruction of the MEMS structures by solution wicking from the wells into the structures.

Theory modified from the coffee ring formation described accurately the drying of hundreds of picoliters of solution drops in a well and capillary system. The accumulation times match between the theory and the experiments with different initial solution concentrations. The solidification rates and profiles also match the theory between different initial concentrations. The 1D numerical model was verified experimentally with five concentrations and eight different groove geometries, using fundamental parameter values. The evaporation rate, J_s , was the lone fitting parameter; however, its value could be determined independently

through advanced thin-film evaporation analysis. While the tests do not span the entire possible design space, the test results do imply that the model can be used to predict behavior of other solvent/solute combinations and groove geometries. The method has proven successful for functionalizing cantilever arrays and has a wide application space that includes functionalization of gas chemical and biological micro-sensors.

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