CONTROLLED PICO-GRAM MATERIAL PLACEMENT ON SUSPENDED STRUCTURES USING SOLUTION WICKING

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ABSTRACT

A fabrication method using inkjet printing of chemically sensitive materials into a suspended microgroove is explored. This involves wicking dissolved polymer into a suspended structure via a capillary groove running its length using surface tension forces. A “well” at the base of the suspended microgroove serves as the target for the inkjet drop. This work presents the theory behind the controlled material dosing, the fabrication method limits and the dried polymer profile measurements in the suspended capillary structures.

INTRODUCTION

There has been a tremendous amount of work in miniaturized gas vapor detectors implementing several detection modes including: chemresistors, chemcapacitors and mass sensors. Arrayed and integrated sensors are needed for total gas analysis and discrimination [1] [2]. Arrayed sensors as well as arraying sensor modes necessitate a single-chip, multi-material fabrication method. Device scale deposition techniques that have been implemented include ink-jet printing [3] [4], micro-capillary deposition [5] and dip-pen nano-lithography [6 Piner]. For this work, drop-on-demand inkjet printing provides rapid ‘functionalization’ and multi-material placement. It is a mask-less process and pL quantities of solution can be deposited. Prior work includes successful deposition of multi-materials on mass-sensitive cantilever arrays using inkjet printing and micro-capillary deposition [5]. However, device scaling and narrow gaps are difficult with these methods.

In contrast, this work addresses a method to make inkjet printing compatible with scaled device size and μm and sub- μm scaled air gaps. This is done by designing a well which serves as the target for the inkjet drop as shown in Fig. 1. A micro-capillary runs the length of the sensor device and upon solvent drying material originally suspended in solution is left in the capillary and on the scaled device.

We have previously shown a mass sensitive (75fg/Hz sensitivity) CMOS-MEMS cantilever oscillator with a 2 μm wide groove running its length as a successful vapor detector (Fig. 2 left) [3]. We explored a further scaled micro-slot cantilever design and showed a 25fg/Hz mass sensitivity (Fig. 2 right) [7]. Both demonstrate the proof of concept behind this method of polymer loading into micron-scaled cantilevers without destruction of the device or the narrow electrostatic gaps. This work addresses the theory, the microgroove aspect ratio limits, and the characterization of the dried polymer profile in the grooves. We demonstrate that this technique is not limited to mass sensitive materials, the solvent used or the concentration of the inkjet drop.

THEORY

The theory of solute transfer in MEMS micro-capillaries is extended from the ‘coffee ring’ formation theory [8]. Consider a solution loaded well and capillary as illustrated in Fig. 1 where the capillary has length, L_c , height, h_c , and width, w_c . The solvent has density, ρ , and an evaporation rate per unit surface area J_s [$\text{kg}/\text{m}^2/\text{sec}$]. The solvent mass rate of change, $\rho \frac{\partial h_c}{\partial t} dx \cdot w_c$

[kg/sec], in the differential element, dx , is described by

Figure 1: (a) Scanning electron micrograph (SEM) of the top view of the well and the capillary. (b) The cross section (A-A') illustrating the well with the inkjet drops and the filled capillary running the length of a MEMS device.

Figure 2: Cross sections of suspended micro-groove (left) and micro-slot (right) with dried polymer.

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

where the first term is the amount of solvent flowing into dx , the second term is the amount flowing out of dx and the final term describes the solvent mass loss due to evaporation from the top surface of the capillary. The velocity profile of the solvent as a function of time, t , and space, x , is described by $v(x, t)$ where $x = 0$ is the entrance from the well into the capillary. The gradient of the velocity profile is described by

$$\frac{dv(x, t)}{dx} = -\frac{J_s}{h_c \rho} - \frac{1}{h_c} \frac{\partial h_c}{\partial t} \Rightarrow \frac{dv(x, t)}{dx} = -\frac{J_s}{h_c \rho} \quad (2)$$

The capillary height, h_c , does not change with time since the volume fill rate of solution from the well due to surface tension forces is much higher than the total volume of solvent evaporated from the capillary. This is a valid assumption for “short” capillary lengths, $L_c < 500 \mu\text{m}$, based on calculations as well as experimental verification.

By similar analysis, the concentration profile, $c(x, t)$ [kg of solute/ m^3 of solvent], is described by

$$\frac{\partial}{\partial t} (c(x, t)) = -\frac{\partial}{\partial x} (c(x, t) v(x, t)) + D \frac{\partial^2}{\partial x^2} c(x, t) \quad (3)$$

Figure 3: Cross section illustrating the drying process in the capillary. The dried solute extends from the end to L_T .

where D is the diffusion coefficient of the solute in the solution. Equations (2) and (3) are two coupled PDEs describing the solute transfer phenomenon with the following boundary conditions

$$\frac{v(0,t)}{dx} = -\frac{J_s}{h_c \rho}, \quad v(L_c, t) = 0 \quad (4a)$$

$$c(0, t) = c_o + \alpha \cdot t, \quad \frac{\partial c(L_c, t)}{\partial x} = 0 \quad (4b)$$

where c_o is the concentration of the inkjet drop and α is a fitting coefficient. Equations (4a) and (4b) indicate that at the end of the capillary channel the solution velocity and the flux of solute are both zero. The solution concentration at the beginning of the channel varies linearly with time. The gradient of the velocity at the beginning of the channel is constant.

In Equation (2), J_s is assumed to be constant for a dilute solution concentration. However, once the concentration reaches a critical concentration, c_r , the solute originally suspended in solution becomes a semi-solid material with solvent diffusing out to the evaporation interface. A concentration dependent evaporation and, thus, velocity gradient describes this transition region

$$\frac{dv(x, t)}{dx} = -\frac{J_s}{h_c \rho} \cdot \frac{1}{1 + \exp[(c(x, t) - c_r)/\mu]} \quad (5)$$

where μ is a transition coefficient.

During the drying process the concentration increases at a higher rate at the end of the capillary channel, L_c . Once the concentration at the end reaches a critical concentration, c_r , the solute once suspended in solution is considered a solid. Once a solid forms the velocity of the solution at this transition point becomes zero. The solute drying process, therefore, begins at the end of the capillary channel then recedes back. Figure 1 shows the profile of the solution in the well and capillary at an initial time, t_o where the drying process has begun. At later times Fig. 3 illustrates what the profile would be where $x = L_T$ denotes the location of the transition between the solution and the solid solute.

RESULTS

Numerical Simulations

Equations (3) and (5) were solved by finite element analysis (FEA) using Comsol Multiphysics. The nondimensional quantities

$$x^* = \frac{x}{L_c}, \quad t^* = A \cdot t, \quad c^*(x^*, t^*) = \frac{c(x^*, t^*)}{c_r}, \quad v^*(x^*, t^*) = \frac{v(x^*, t^*)}{AL_c} \quad (6)$$

$$A = \frac{J_s}{h_c \rho} \quad (6a)$$

are substituted in Eqns. (3) and (5) to form the normalized coupled partial differential equations

$$\frac{dv^*(x^*, t^*)}{dx^*} = -\frac{1}{1 + \exp\left[\frac{c_r}{\mu} (c^*(x^*, t^*) - 1)\right]} \quad (7)$$

$$\frac{\partial}{\partial t^*} (c^*(x^*, t^*)) + \frac{\partial}{\partial x^*} (c^*(x^*, t^*) v^*(x^*, t^*)) - \frac{D}{AL_c^2} \frac{\partial^2}{\partial x^{*2}} c^*(x^*, t^*) = 0 \quad (8)$$

Channel length, L_c	120 μm
Channel height, h_c	3.2 μm
Solvent density, ρ	1500 kg/m^3
Solute diffusion:evaporation ratio, D/J_s	$10^{-8} \text{ m}^4/\text{kg}$
Initial solution concentration, c_o	5 kg/m^3
Solution to solid transition concentration, c_r	1000 kg/m^3
Well concentration fitting coefficient, α	1.3 $\text{g/m}^3/\text{sec}$
Transition coefficient, μ	50

Table 1: Channel dimensions and solution material properties.

Figure 4: Concentration profile, $c^*(x^*, t^*)$ at different times, t^* .

The parameters listed in Table 1 are used in the numerical analysis. Figure 4 shows the normalized concentration profiles along the capillary channel length at varying times during the drying process. The concentration increases at a higher rate at the end of the channel. At later times there is a large transition in the concentration. This is where L_T is located.

Experiments

An array of suspended microgroove capillaries was fabricated using post-CMOS (Jazz 0.35 μm BiCMOS) fabrication steps [3]. The final step involves polymer deposition using inkjet printing into the target well area. Three drops of 5 kg/m^3 of polythiophene suspended in trichlorobenzene (TCB) were deposited at the base of the suspended capillary with width, height, and length of 2 μm , 3.2 μm and 120 μm , respectively. Trichlorobenzene is the solvent chosen for the experiments because of its “low” evaporation rate. Solvents with higher vapor pressures evaporate too fast to track the evaporation process with the current experimental setup. Figure 5 shows the snapshots in time of the solution drying. An arrow in each picture indicates the solution-solid transition region, L_T .

Video images of the drying process were taken at 10 frames per second. In each frame the transition between the ‘light’ and ‘dark’ portion in the channel is tracked. The initial concentration of the drop, c_o , was varied. The transition region was monitored for three drops with varying initial concentrations: 0.5 kg/m^3 , 1 kg/m^3 , 2.5 kg/m^3 , 5 kg/m^3 and 7.5 kg/m^3 . Figure 6 shows the normalized transition region location as a function of time for the various solution concentrations. Both the measured and the FEA model using $A = 2.5$ are shown. There are two regions to note: an ‘accumulation region’ where there is some initial time for the solid solute to form at the end of the channel and the ‘solidification region’ where the transition location decreases with time. For the FEA data, the ‘accumulation region’ is located at $t < 31$ sec, $t < 28$ sec, $t < 13.5$, $t < 7.5$ sec and $t < 5$ sec for the 0.5 kg/m^3 , 1 kg/m^3 , 2.5 kg/m^3 , 5 kg/m^3 and 7.5 kg/m^3 concentrations, respectively. For the measured data, this region is only seen with concentrations of 0.5 kg/m^3 , 1 kg/m^3 , 2.5 kg/m^3 at the respective times of $t < 40$ sec, $t < 26$ sec and $t < 12$ sec. The ‘solidification region’ begins after these respective times.

Figure 5: Images of the well and the suspended capillary ($2 \mu\text{m}$ width, $3.2 \mu\text{m}$ height and $120 \mu\text{m}$ length) 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 .

Figure 6: The measured transition location, L_T , after 3 solution drops of polythiophene in TCB with varying c_o . This is compared with the FEA model ($A = 2.5$).

Figure 7: The measured and FEA solidification rate, $|dL_T/dt|$, versus the initial drop concentration.

Figure 8: Polymer extent and corresponding mass after solvent drying with 1 kg/m^3 of solution concentration.

At the initial measurement time, there is an apparent offset between the measured and FEA L_T . This is an artifact of the optics for the 0.5 kg/m^3 , 1 kg/m^3 and 2.5 kg/m^3 concentrations. However, for the larger concentrations the solidification begins at a time before the initial measurement time. During solidification, the measured fill rate digresses from the model at approximately $t > 45$ sec for the 1 kg/m^3 concentration, $t > 55$ sec for the 2.5 kg/m^3 concentration, and $t > 35$ sec for the 2.5 kg/m^3 , 5 kg/m^3 and 7.5 kg/m^3 concentrations. This is probably due to a non-linear increase in concentration in the well area.

A small ‘dark’ region was observed at distances close to the solidification front, L_T . This region merges with the solidification front at later times during the drying process. This merger is seen as a ‘flat’ region in the curves in Fig. 6. This flat region is observed at times equal to 58 sec, 45 sec, 68 sec and 63 sec for the 0.5 kg/m^3 , 1 kg/m^3 , 5 kg/m^3 and 7.5 kg/m^3 .

The fill rate magnitude, $|dL_T/dt|$, is shown in Fig. 7 and compared to the model for varying initial concentrations. The measured fill rates are calculated between the time when the solidification begins and the merging time. For the FEA data, the rates indicated in Fig. 7 are calculated at the times shortly after solidification.

The number of drops was varied using an initial concentration of 1 kg/m^3 and the final L_T was measured after complete solvent drying (see Fig. 8). The corresponding mass of the loaded material is indicated in the figure. With a proper number of drops the dried solute extent from the end of the channel can be set. This method provides controlled material placement from dilute solutions with a 100 pico-gram per drop resolution with a 1 kg/m^3 initial concentration.

Capillary structures with varying groove aspect ratios and $200 \mu\text{m}$ lengths were fabricated and the solidification front was monitored using 3 drops of 5 kg/m^3 of polythiophene in TCB with each of the structures. The fill rate versus channel width with two channel heights, h_c , is shown in Fig. 9. There is a large aspect ratio dependence on the drying process. The meniscus of the liquid in the capillary has a large effect on the drying process and the solidification rate. The effective evaporation rate per unit surface area is observed to be larger with larger aspect ratio structures where the aspect ratio $= h_c/w_c$. In Fig. 9, the solidification rate dependence on the channel width varies with the channel height.

Figure 9: The measured solidification rate using 3 drops of 5 kg/m³ in channels with varying aspect ratios.

Figure 10: Top (a & b) and angled (c & d) SEM views of 1.8 μm and 10.5 μm wide grooves. The height for both structures is 3.2 μm.

Figure 11: Measured polymer profile at the base and tip for the 1.8 μm wide (left) and 10.5 μm wide (right) grooves.

Profile measurements

The scanning electron microscope images of two grooves with different aspect ratios are shown in Fig. 10 after solute solidification. The chip was sputter coated with gold for SEM contrast. The groove widths are 1.8 μm and 10.5 μm. Both grooves have 3.2 μm heights. The final polymer extent, L_T , is visible for the 10.5 μm groove (Fig. 11b). Profile measurements were taken using a white light interferometer. These are shown in Fig. 11. The profile of the dried material is dependent on the capillary groove aspect ratio. The meniscus effect is evident with the wider groove. There is more dried material along the channel sidewalls with the wider groove indicating that the 2-D evaporation profile must be considered with wider grooves. A maximum width for sustained capillary action was measured to be 7 μm and 14 μm for the 1.6 μm and 3.2 μm tall grooves,

respectively. At larger widths the solution fills and dries in the corners of the grooves.

CONCLUSIONS

Inkjet printing into micro-capillaries is a viable mechanism for controlled, repeatable material placement. The theory of solute transfer in MEMS micro-capillaries is extended from the 'coffee ring' formation theory. The numerical analysis from the theory matches qualitatively with the experimental measurements of the 'accumulation region' and the solidification front. The experiments and FEM simulations verify that Eqn. 5 is a viable approach to handling the evaporation rate in the solution to solid transition regime. The accumulation time and the solidification rate are dependent on the initial concentration used.

Further experiments and analyses are needed to quantify two effects: the concentration change with time in the well and the evaporation rate dependence on the meniscus. The solution concentration in the well was assumed to be linear for the current model. However, it is evident that at later drying times this is not the case. This is probably due to the change in the exposed surface area at the times when the well begins to run out of solution. At these times the well is partial filled with solution.

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REFERENCES

- [1] D. Lange, C. Hagleitner, A. Hierlemann, O. Brand, and H. Baltes, "Complementary Metal Oxide Semiconductor Cantilever Arrays on a Single Chip: Mass-Sensitive Detection of Volatile Organic Compounds", *Analytical Chemistry*, 74, 13, (2002).
- [2] J. R. Stetter and W. R. Penrose, "Understanding Chemical Sensors and Chemical Sensor Arrays (Electronic Noses): Past, Present, and Future", *Sensors Update*, 4, (2002).
- [3] S. S. Bedair and G. K. Fedder, "Polymer wicking to mass load cantilevers for chemical gravimetric sensors," *IEEE Transducers '05*, Seoul, Korea, pp. 2035-9.
- [4] P. Cooley, D. Wallace and B. Antohe, "Applications of ink-jet printing technology to BioMEMS and microfluidic systems", *SPIE Conf. on Micromachining and Microfabrication*, 2001.
- [5] A. Bietsch, J. Zhang, M. Hegner, H. P. Lang, and C. Gerber, "Rapid functionalization of cantilever array sensors by inkjet printing", *Nanotechnology*, 15, (2004).
- [6] R. D. Piner, J. Zhu, F. Xu, S. Hong and C.A. Mirkin, "Dip Pen' Nanolithography", *Science*, 283, 661 (1999).
- [7] S. S. Bedair and G. K. Fedder, "Polymer mass loading of CMOS/MEMS microslot cantilever for gravimetric sensing", *IEEE Sensors '07*, Atlanta, Georgia, pp 1164-7.
- [8] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, "Contact line deposits in an evaporating drop", *Physical Review E*, 62, 1, (2000).