



# Active control of evaporative solution deposition by means of modulated gas phase convection



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## ABSTRACT

In solution processing, functional materials are dissolved or dispersed in a solvent and deposited typically as a thin liquid film on a substrate. After evaporation of the solvent, a dry layer remains. We propose an 'active', non-contact technique for evaporative pattern formation that does not require any substrate modification. It is based on an array of nozzles, some of which introduce a dry carrier gas in the air space above the liquid film. By spatially modulating the solvent vapor saturation above the liquid, patterns in the dry layer thickness can be induced in a controlled fashion. In this manuscript we study pattern formation due to a single pixel of such a nozzle array, by means of quantitative experiments and numerical simulations.

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## 1. Introduction

In the past decades a wealth of different methods has been developed for pattern formation in liquid suspensions and solutions such as illumination with visible [1–4], ultraviolet [5] and infrared light [6–12] as well as application of magnetic [13–18] and electric [19–29] fields.

Routh and Russel [30] presented a model for the drying of thin films of aqueous Latex particle suspensions. They also conducted experiments regarding pattern formation in an initially uniform film via locally hindering evaporation by a cover with regularly spaced holes. Later this technique became known as *evaporative lithography* [31–40]. Arshad and Bonnecaze [41] introduced *templated* evaporative lithography, where a solvent-permeable membrane of non-uniform thickness is put not above the liquid dispersion film, but rather in direct contact with it. In both cases, the evaporative solvent vapor flux is spatially modulated in a passive fashion by introducing a position-dependent resistance to evaporative mass transfer. Georgiadis et al. pointed out that one of the limitations of evaporative lithography is the retarding effect of the mask on the overall evaporation rate, leading to long process times [11].

We propose an 'active', non-contact technique for evaporative pattern formation that is based on an array of nozzles, some of which introduce a dry carrier gas in the air space above the liquid

film (see Fig. 1(a)). In this fashion, evaporative mass transfer is enhanced by reducing and spatially modulating the solvent vapor saturation in the gas phase above the liquid film. A local balance between positive and negative flow rates (i.e. between neighboring nozzles that respectively introduce dry gas and suck away solvent-vapor saturated gas) can prevent undesirable, gas-flow-induced solute redistribution over distances exceeding the array period.

This technique is compatible with moving substrates - as required e.g. for roll-to-roll processing [42–45] of organic electronic devices - if the gas flow distribution is made time-dependent in accordance with the substrate displacement. In this manuscript, however, we consider stationary substrates and focus on pattern formation induced by a single pixel of such a nozzle array. This allows us to characterize the pattern formation process comprehensively by a combination of well-controlled experiments and numerical model simulations.

## 2. Experimental section

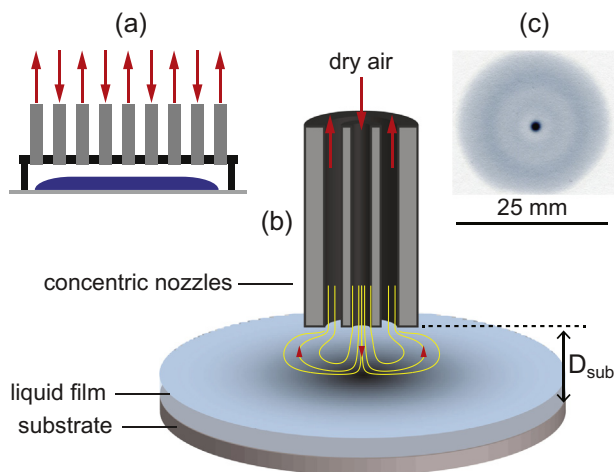
Fig. 1(b) shows a schematic of the experimental setup. A liquid film of an aqueous dispersion of poly(3,4-ethylene-dioxythio phene):poly(styrenesulfonate) (PEDOT:PSS, initial concentration of 0.51 wt%, without co-solvents and surfactants, supplied by Agfa-Gevaert N.V.) nanoparticles was prepared on a chemically patterned substrate. Glass substrates (with a size of 75 × 50 mm and a thickness of approximately 1 mm) were cleaned by subsequent immersion into a detergent solution (Contrad 70), deionized water, acetone, ethanol and isopropanol in an ultrasonic

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### Nomenclature

$r, z$	coordinates, m	$p_{\text{air}}$	value of $p$ at liquid-air interface, Pa
$D_{\text{film}}$	nozzle height w.r.t. liquid-air interface, m	$s$	solvent vapor concentration, $\text{kg}/\text{m}^3$
$D_{\text{sub}}$	nozzle height w.r.t. substrate, m	$s_{\text{sat}}$	saturation concentration, $\text{kg}/\text{m}^3$
$Q$	flow rate, $\text{m}^3/\text{s}$	$J_0$	pure solvent evaporation flux, $\text{kg}/(\text{m}^2 \text{ s})$
$R_1$	inner radius of inner nozzle, m	$J$	solution evaporation flux, $\text{kg}/(\text{m}^2 \text{ s})$
$R_2$	outer radius of inner nozzle, m	$\tau_{\text{air}}$	shear stress at liquid-air interface, Pa
$R_3$	inner radius of outer nozzle, m	$\rho_{\text{air}}$	air density, $\text{kg}/\text{m}^3$
$R_4$	outer radius of outer nozzle, m	$\mu_{\text{air}}$	air viscosity, Pa s
$h$	liquid film thickness, m	$D_{s,\text{air}}$	diffusion coefficient of solvent vapor in air, $\text{m}^2/\text{s}$
$h_i$	initial value of $h$ , m	$H_{\text{rel}}$	relative humidity, %
$h_{\text{dry}}$	dry film thickness, m	$\vec{n}, \vec{t}$	unit normal and tangential vectors
$h_{\text{sol}}$	solute thickness, m	$\vec{v}$	liquid velocity, m/s
$c$	solute concentration, wt%	$\vec{v}_{\text{int}}$	velocity of liquid-air interface, m/s
$c_i$	initial value of $c$ , wt%	$\rho_{\text{liq}}$	liquid density, $\text{kg}/\text{m}^3$
$c_{\text{max}}$	maximum value of $c$ , wt%	$\mu_{\text{liq}}$	liquid viscosity, Pa s
$c_{\text{top}}$	value of $c$ at liquid-air interface, wt%	$\gamma$	surface tension, N/m
$\langle c \rangle$	$c$ averaged over $h$ , wt%	$D_{\text{liq}}$	diffusion coefficient of solute in solvent, $\text{m}^2/\text{s}$
$r_d, z_d$	computational domain dimensions, m	$\vec{g}$	gravitational acceleration, $\text{m}/\text{s}^2$
$\vec{u}$	gas phase velocity, m/s	$Co$	contrast of solute deposit
$ \vec{u} _{\text{max}}$	maximum gas speed, m/s	$w$	width of solute deposit, m
$p$	pressure, Pa		



**Fig. 1.** (a) Sketch of an active evaporative lithography process. An array of nozzles provides local control of the solvent vapor saturation above an evaporating solution layer. (b) Sketch of the experimental setup (not to scale).  $D_{\text{sub}}$  denotes the distance between the bottom of the concentric nozzles and the top of the substrate. Dry air is pumped at a constant flow rate through the inner needle, humid air is removed through the outer needle at the same flow rate. The red arrows indicate the direction of the flow in the inner and outer needle. The yellow curves represent streamlines of the induced air flow. (c) Optical transmission image of a typical dry solute distribution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Two concentric nozzles (Linari Engineering, product number COAX\_2DISP), consisting of an inner needle (inner radius  $R_1 = 0.25$  mm, outer radius  $R_2 = 0.42$  mm) and an outer needle (inner radius  $R_3 = 0.69$  mm, outer radius  $R_4 = 0.92$  mm) was placed above the center of the liquid film. The substrate was placed on a Kohzu ZM10A-C3C z-translation stage, which allowed precise control over  $D_{\text{sub}}$ , the distance between the bottom of the nozzle and the top of the substrate. This distance was measured with a Mitutoyo ID-C125B digital indicator. Dry air (Linde, product number 3580110,  $\text{N}_2/\text{O}_2$  mixture, humidity level  $\leq 5$  ppm) was supplied through the inner needle (the arrows in Fig. 1(b) indicate the flow direction). For flow rates  $Q$  lower than 4 ml/min, a large-volume syringe (Hamilton, product number 86020, 100 ml) placed on a syringe pump (KDS Gemini 88) was used to drive the flow. During a typical measurement, the syringe was refilled with dry air a few times. For larger flow rates, the flow was controlled with a needle valve and measured with a flow meter (Omega, FMA3301ST). The outer needle extracted air, with a flow rate equal to that through the inner needle. During the experiment, the substrate and the nozzle were covered with a transparent enclosure. After evaporation of the solvent, the dry layer thickness profiles  $h_{\text{dry}}(x, y)$  were obtained by measuring the optical absorption profiles  $A(x, y)$  in a transmission configuration. Fig. 1(c) shows a typical example of the dry film thickness distribution after solvent evaporation. The black dot in the center, of approximate diameter 1 mm, corresponds to the induced solute accumulation, which gives rise to stronger absorption.

### 3. Numerical model

We have developed a numerical model to study the effect of the modulated gas phase convection on the solution deposition process. The model consists of two different parts. In the first part, the gas phase model (Section 3.1), we solve for the velocity of the air and the solvent vapor concentration in the vicinity of the nozzles. From this model, we obtain the pressure  $p_{\text{air}}(r)$  and shear stress  $\tau_{\text{air}}(r)$  exerted by the air flow. These quantities are inserted in the second model, the liquid film model (Section 3.3), where we solve for the transport of the solute in the liquid film. The (uncorrected) solvent vapor flux  $J_0(r)$  is determined from the first

bath for 15 min each. The substrates were dried using a nitrogen jet. A monolayer of 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) was applied on the substrate by immersion in a PFOTS-heptane solution for 2 min, followed by immersion in pure heptane and rinsing with de-ionized water. The substrate, now with a hydrophobic surface, was covered with a mask (2 mm thick metal plate with a 25 mm diameter circular opening) and placed in a UV/ozone cleaner (Jelight model 42-220) for 15 min. This rendered the region underneath the circular hole fully hydrophilic. The PEDOT:PSS dispersion was deposited on the hydrophilic pattern using a Hamilton syringe. The chemical pattern allowed for a reproducible initial wet layer thickness.

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