Evaporation of thin liquid films on chemically patterned surfaces[1]

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Introduction

Evaporative material redistribution, known as the "coffee-stain effect" [1] is caused by contact line pinning and the non-uniformity of the evaporation rate in the vicinity of contact lines. This topic is of considerable industrial interest e.g. in the context of solution-based, roll-to-roll deposition processes of organic semiconductors for applications in large-area electronics. Quantitative understanding and control of solvent evaporation is of crucial importance, since it can lead to undesirable material redistribution and uneven film thicknesses primarily near corners and edges of device structures. Towards a better understanding of this process, we have studied the evaporation of pure solvents on chemically patterned surfaces. For nominally pure isopropanol (IPA) we observed a number of instabilities on rectangular stripes and studied them as a function of the stripe width.

Experimental procedure

For our experiments we used Si wafers that were cut into 5 x 5 cm^2 pieces, then thoroughly cleaned first with a 1:1 solution of H_2S0_4 and $(30\%)H_2O_2$ (piranha) and then treated with oxygen plasma for 30 s. The chemical patterning [2] was defined by means of photolithography. After development and baking, the samples were immersed in a ~1mM solution of perfluorooctyl-trichlorosilane (PFOTS, Sigma Aldrich) in toluene for 10 min, after which they were rinsed with neat toluene, blown dry and the photoresist stripped off. The length of the chemically defined hydrophilic stripes was 4 cm, whereas the width varied from 0.5 to 2 mm.

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The evaporation experiments were carried out in a custom-made sample holder (Fig. 1) that provides a uniform laminar flow over the entire surface area of the samples. Due to a shallow cavity in the middle of the holder, the top surfaces of the samples are flush with the surrounding bottom surface of the sample holder. The holder is mounted on top of a brass block that is thermostatted by means of water circulation from a constant temperature bath kept at either 20°C or 25°C. A lid with a glass window was placed on top of the sample holder to seal it and provide a controlled environment. Two grades of IPA were used: HPLC grade (99.9%, Sigma-Aldrich) and Finyte grade (99.8%, J.T. Baker) with the nominal material properties of surface tension γ(T=20°C) = 23 mN/m, density ρ(20°C) = 786 kg/m^3 and viscosity μ(20°C) = 2.46 mPa-
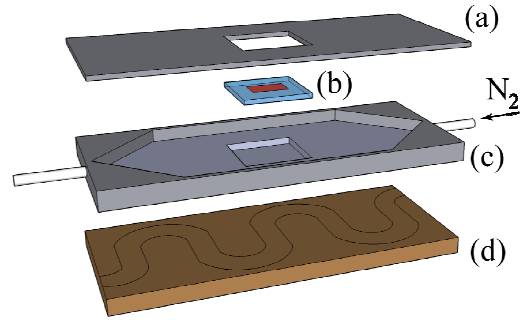
Fig 1: *Evaporation setup: protective lid with thin glass window (a), patterned sample (b), laminar flow sample holder (c) and thermo-statted brass block (d)*

s. A flame-cleaned glass pipette was used to deposit the IPA. All experiments were conducted at room temperature and recorded using a CCD camera on top of an Olympus BX51 microscope equipped with a 750nm bandpass filter. The microscope resides inside a laminar flow-hood which provides filtered air flow to minimize dust contamination. Nitrogen flow with a rate of 30.2 ml/min was applied parallel to the stripes, resulting in an average gas velocity of 1.5 mm/s above the samples. Due to the high thermal conductivity of Si of $k_{Si} \approx 130$ W/(m-K), the effective Biot number was very small and the sample temperature remained uniform during experiments.

Experimental observations

We observed 3 types of instabilities and named them corner-, edge- and centerline- instabilities.

Rivulet centerline instability: After deposition the initial height profile of the liquid was more or less homogeneous along the hydrophilic stripe. As time progressed it thinned in the middle and flowed towards the stripe ends, as sketched in Fig. 2 (bottom). After a large fraction of the

deposited IPA has evaporated, a more or less periodic arrangement of local maxima of the film thickness is observed (Fig. 2) with a characteristic wavelength comparable to the width of the stripe. Our hypothesis was that the mechanism driving the instability is evaporation-induced thermocapillary stresses and that capillary and hydrostatic pressures constitute opposing forces. We conducted a
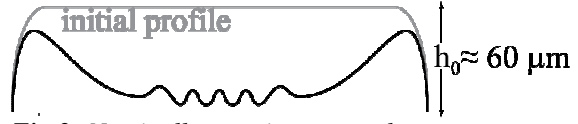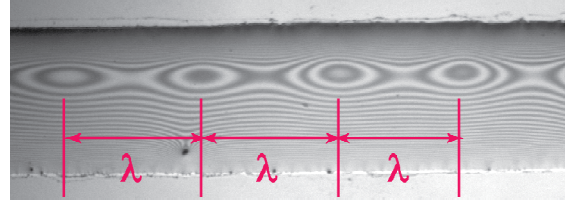
Fig 2: Nominally pure isopropanol evaporates on a rectangular hydrophilic patch (w = 0.75 mm) on a Si substrate in the absence of N_2 flow (T=20°C). Periodic local maxima are observed along the centerline of the stripe as visualized by the optical interference fringes.

linear stability analysis based on the lubrication equation for thin film flows [3] to identify the influence of the pattern width on the instability wavelength and found the following expression for the maximally unstable wavelength

$$\lambda_{max} = 2\pi \left[\sqrt{\frac{9}{2}\left(-\frac{105}{256\gamma h_0}\frac{\partial \gamma}{\partial T}\frac{q_2 L}{k_{liq}} - \frac{1}{w^2} - \frac{\rho g}{9\gamma} \right)} \right]^{-1}$$

Here, k_{liq} = 0.14 W/(m-K) is the thermal conductivity of IPA, $\partial \gamma/\partial T$ = -0.0789 mN/(m-K) is the temperature coefficient of surface tension. We used a quasi-steady, diffusion-limited evaporation model to determine the evaporative mass flux $J(y)$. The parameter q_2 corresponds to a weighted average of $J(y)$ over the rivulet cross-section, which we approximated as parabolic. Insertion of all relevant geometric parameters and material properties, however, pointed at linear stability of narrow IPA rivulets. That suggests that a factor not taken into account is responsible for the observed instability. When a higher purity grade of IPA was used (HPLC, 99.9%), the height modulation which we termed centerline instability was either smaller or absent, which indicates that solutocapillary effects may play a decisive role. We are currently working towards incorporating solutocapillary effects into our linear stability model.

Edge and corner instabilities: Different types of instability were observed near edges and corners of the stripe patterns also for the HPLC grade of IPA (Fig. 3). After evaporation of a significant

fraction of the initially deposited IPA, series of small-scale perturbations with a spacing on of order 50 μm are observed in the vicinity of the stripe edges [lower right corner of Fig. 3(b)]. There the local film thickness is very small, such that the temperature of the liquid-air interface is close to the substrate temperature, due to the large value of k_{Si}. This renders a thermocapillary origin of the instability unlikely. Later, when the overall height of the rivulet and thus the
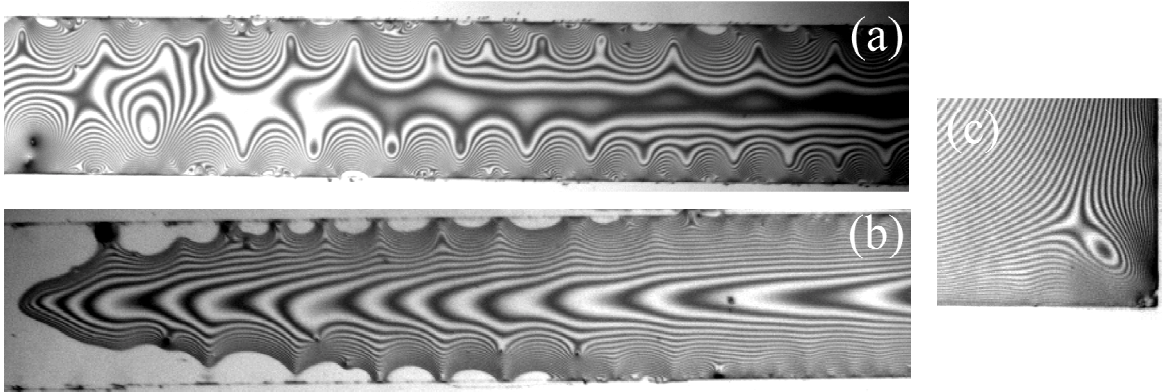
Fig 3*: (a,b) Edge instability patterns observed on 0.5 mm wide stripes. (c) Local film thickness maximum near a corner of a 1.75 mm wide stripe (image height 0.65 mm). In all cases the temperature was T=25°C and air-flow was present from left to right.*

capillary pressure has decreased, undulations with a larger average wavelength were formed [Fig. 3(a)]. Upon recession of the rivulet from the stripe ends, it adopts a shape reminiscent of a serrated blade [Fig. 3(b)]. Figure 3(c) shows a local film thickness maximum near a corner of a hydrophilic stripe. Its morphology is very similar to some of the protrusions near the lower stripe edge in Fig. 3(a), such that their origins are likely identical. We hypothesize that solutocapillary stresses due to the presence of trace amounts of less volatile components with a higher surface tension are the cause of all instabilities observed. This hypothesis is supported by Fig. 3(b), where less- or non-volatile deposits are visible at the stripe edges preferentially at the locations where protrusions had formed. We will test this hypothesis by means of numerical model calculations.

References

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