Pattern formation by capillary instabilities in thin films

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Chapter 6

Lithographic Techniques
Using External Fields

6.1 Introduction

The stability of thin polymer films is very important in many technological applications. Ranging from photo–lithography to coatings, the ability to de-
posit stable films with uniform thickness is crucial. In general, thin films are
stable against capillary fluctuations at their surfaces. In the absence of hetero-

genieties, thin non–wetting films may be destabilised by van der Waals (vdW)
and other forces [1]. Because these interactions are relatively weak and short
ranged, films thicker than $\sim 20 \text{ nm}$ are typically stable. To destabilize thick
films, long–range forces such as electrostatic or temperature gradient induced
forces must be applied to the polymer–air interface [2, 3].

The application of an external force permits to control the instabilities, if the magnitude of the force can be varied. Our lithographic technique ex-
ploited a spontaneous structure formation process and decreased its length
scale to technologically interesting features sizes. The ability to fabricate
nanostructures is essential in the development of functional devices that incorporate nanoscale features. Hence, non–photolithographic methods could provide technologically simpler and cheaper nanofabrication routes. In this chapter, an extension of the electrohydrodynamic (EHD) technique is presented that allowed us to produce structures in the range of 100 nm. The influence of several factors such as film thicknesses, field strength, imposed periodicity, etc. on the lithographic technique are presented.

### 6.2 Classical EHD Lithography

Schäffer et al. developed a new lithographic technique that uses electrostatic forces to control the initial film instabilities [2]. When applying an electric field normal to the interface between two dielectric materials with different polarizabilities, an interfacial electrostatic pressure arises from the uncompensated displacement charges. This pressure couples to the capillary wave spectrum of the liquid interface. A narrow band of wavelengths is amplified, destabilizing the interface. The most unstable wavelength is characteristic of the interfacial force balance, where the Laplace pressure acts as a restoring force. The generic experiment is schematically depicted in Fig. (6.1).

The setup used by Schäffer et al. consisted of a ≈ 100 nm thin polymer film, deposited by spin–coating on a substrate that served as one of the electrodes. Facing the polymer layer, a second electrode was placed at distance \( d \) from the first one. The initial film thickness was \( h < d \). The film was liquified by heating to a temperature higher than its \( T_g \) and a voltage was applied to the electrodes. Due to the small distance between the electrodes the generated electric field was extremely high (\( E \sim 10^7 \text{V} \cdot \text{m}^{-1} \)). The instability was given time to develop and after a period that ranged from several hours to a couple of days, the formed structure was frozen by quenching the entire setup to room temperature. The upper electrode was mechanically removed and the sample was investigated by optical and atomic force microscopy. To facilitate the disassembly of the device, the surface of the upper electrode was covered with a self–assembled alkane monolayer.

Typical experimental results are shown in Fig. (6.1). The initial capillary film undulations (Fig. 6.1a) were amplified by the electrostatic pressure. They grew and eventually touched the upper electrode forming columns (Fig. 6.1b). Changing the system parameters (applied voltage, distance between
6.2 Classical EHD Lithography

Figure 6.1: Schematic representation of the EHD setup. A liquid polymer film is destabilized by an electrostatic pressure, which is a consequence of the applied electric field. Depending on the voltage $U$, the electrode spacing $d$, the initial film thickness $\ell$, the dielectric constant $\epsilon_p$, and the surface tension $\gamma$, a narrow distribution of wavelengths $\lambda$ is amplified. The optical micrographs are a) $5 \times 5 \mu m^2$ and b) $30 \times 30 \mu m^2$.

electrodes, initial film thicknesses) the density and size of the columns could be varied.

To induce the morphological features showed in Fig. (6.1b), a laterally homogeneous electric field was used. By utilizing laterally variable electric fields, Schäffer et al. developed a lithographic technique that harnessed the initial film instability to replicate patterns with extremely high fidelity. The process is schematically depicted in Fig. (6.2)

Instead of planar electrode, a topographically structured upper plate\footnote{The master electrode was produced by “writing” the structures with an electron beam.} was used (Fig. 6.2a). The variation of the plate spacing $d$ due to the electrode
topography results in a variation of the force field. Therefore, the lateral inhomogeneous field focusses the instability towards regions of highest electric field where the electrostatic pressure has a higher magnitude (i.e. underneath the protuberances). Furthermore, the time constant associated with this process is much smaller underneath the structures, so that the polymer is destabilized first at the regions where $d$ is smallest. This leads to the replication of the electrode topography, which is transferred into the polymer film (Fig. 6.2b and c).

### 6.3 Hierarchical Structure Formation in E–Fields

Similar to most other lithographic methods, the method described in Section 6.2 structures a single layer of polymer. For many applications, however, it is desirable to control the spatial arrangement of more than one component. With traditional methods, this process requires an iterative, multistep pro-
Figure 6.3: Model of the hierarchic structure formation process. a) Starting from a polymer bilayer, the polymer—air surface is first destabilized by an electric field generated by the applied voltage, $U$. The initial instability results in the formation of columns spanning from the surface of the lower layer to the top electrode. b) During the column–formation process, the bottom polymer layer is deformed at the polymer–polymer—air contact line. c) In a secondary instability, the deformation of the lower layer is enhanced by the electric field, driving the polymer upward on the outside of the columns. d) In the final configuration, the polymer of the lower layer has formed a mantle around the primary columns.

procedure, making the replication more complex and less reliable. To overcome such disadvantages we developed a replication process that simultaneously structures multiple materials. By exposing a bilayer of two different polymers (polystyrene and polymethylmetacrylate) to an electric field perpendicular to the dielectric interfaces, electrohydrodynamic instabilities at both polymer surfaces produced a hierarchic lateral structure.

Instabilities at both polymer–air and polymer–polymer interfaces were also studied previously [2, 3, 4]. The structure formation stemming from a combination of dewetting and electrostatic forces was shown to yield a rich pattern
formation process \[^{[5]}\]. The forces acting on the dielectric interfaces of the polymer–polymer–air trilayer generates instabilities at these interfaces with different characteristic time constants. Consequently, the interfaces are destabilised at different times, leading to a lateral redistribution of both materials. The resulting hierarchy of length scales in these structures can be harnessed in a novel lithographic technique. The formed structures exhibited two independent characteristic dimensions: one dictated by the master electrode and a second one dictated by the instability of the bottom polymer layer.

Our approach is schematically shown in Fig.(6.3). Thin films of poly methyl methacrylate (PMMA) \((M_w = 90 \text{ kg/mol}, \frac{M_w}{M_n} = 1.07)\) and polystyrene (PS) \((M_w = 100 \text{ kg/mol}, \frac{M_w}{M_n} = 1.06)\) with thicknesses of 150 nm and 100 nm, respectively, were spin–coated from 3% solutions in toluene onto highly polished silicon wafers. The substrates were cleaned prior film deposition with “Snow–jet” and then immersed for 30 minutes in “Piranha” solution, followed by a thorough wash in Millipore water.

The PS film was floated onto a pool of deionized water and then transferred onto the PMMA layer to form a PS/PMMA bilayer. The sample was subsequently placed into an oven at 70\(^\circ\)C for two hours to remove the residual water. A silicon wafer (planar – as in Fig.(6.3a) – or with a design topography) was mounted facing the polymer bilayer, leaving an air–gap. To facilitate the disassembly of the device, a self–assembled organic monolayer was deposited onto this wafer prior to the experiment. It also ensured that no polymer remained on this electrode after disassembly. The distance \(d\) between the electrodes typically varied by a few micrometers over a lateral distance of 1 cm, giving rise to a wedge geometry. The assembly was placed between two pieces of copper, which were connected to a voltage–stabilized power supply. To facilitate good electrical contact between the copper electrodes and the silicon plates, the backside of the wafers were coated with a thin gold layer \((\approx 100 \text{ nm})\) and then covered with electrically conducting paste.

The capacitor assembly was placed into an oven set to a temperature of 170\(^\circ\)C for approximatively 24h at an applied voltage of 50 V, corresponding to an electric field of \(\sim 1 \times 10^8 \text{ V/m}\). To obtain a snap–shot of the formed structure, the sample was rapidly quenched to room temperature before removing the electric field. The sample was analyzed by optical microscopy (Olympus optical microscope BX60) and tapping mode atomic force microscopy (AFM) (Digital Instruments D3100) directly after device disassembly. These images
6.3 Hierarchical Structure Formation in E–Fields

Figure 6.4: Instabilities of a PMMA–PS–air trilayer in an electric field. a) Low-resolution optical micrograph showing an overall columnar morphology. The AFM images in b) and c) show a single column before and after removing the PS phase by washing the sample in cyclohexane. The PMMA phase in b) forms a mantle around the PS column with a height of \(\sim 170\) nm and a width of \(\sim 200\) nm.

reflected the lateral distribution of both PS and PMMA on the substrate. Subsequently, the PS was removed by washing the sample in cyclohexane (good solvent for PS, but not for PMMA) for \(\sim 3\) h at 35\(^{\circ}\) C. The distribution of the remaining PMMA structure could then be determined independently. A typical image of a polymer bilayer that was heated between planar electrodes is shown in Fig.6.4a).

When using a planar electrode, the lateral distribution of the polymers was similar to Fig.6.1a. Fig.6.4a) represents a low magnification optical micrograph of the electric field “molded” columns that span the two electrodes. The AFM scan of a single column in Fig.6.4b) shows a distinct rim which does not exist when using a single–layer film. Washing the sample in cyclohexane significantly enhances the rim and reveals that the composition of the columns consist of a cylindrical PS core surrounded by PMMA. Fig.6.4c) shows the
Figure 6.5: Pattern replication by a hierarchical instability. By using a topographically structured electrode (inset in a), the structure-formation process shown in Fig. (6.4) can be controlled to laterally replicate the structure of the electrode. The optical micrograph in a) shows an overview of a line pattern replicated by the electrohydrodynamic instability. The AFM image in b) shows five replicated lines. After removing the PS phase by washing the sample in cyclohexane, the secondary PMMA structure is revealed in the scanning electron micrograph in c) (height: 160 nm, width: ∼100 nm).

column after PS removal. The width of the PMMA shell (∼200 nm) was significantly smaller than the overall column diameter of ∼3.4 µm.

The structure formation of the columns in Fig. (6.4a), can be understood in terms of a sequential electrostatic destabilization of the polymer bilayer. The process is schematically depicted in Fig. (6.3a–d). The upper PS layer destabilizes initially, forming columns that span from the surface of the lower layer to the upper electrode. As the PS retracts into the columns, the PMMA layer is exposed to air. At the polymer–polymer–air contact line the PMMA film is deformed. These deformations nucleate a secondary instability causing the material of the lower layer to “climb–up” along the primary PS columns.

To determine which layer is destabilized first, the force balance at both
interfaces and the hydrodynamic flow in both films have to be considered. Both the PMMA–PS interface and the PS–Air surface are destabilized by the applied electric field. According to Eqn.(2.48) in Section 2.3.3 of this thesis, the characteristic time constants \( \tau \) for the PS–PMMA and PS–air interfaces determine which interface is destabilized first. \( \tau \) depends on two factors: \( (i) \) the force balance at the interface and \( (ii) \) the flow of material in the polymer layers, characterized by the polymer viscosities.

From Eqn.(2.35) in Section 2.3.2, the destabilizing electrostatic pressure at the PS–air surface is larger than at the PS–PMMA interface. This difference in the destabilizing force is compensated by a larger restoring force at PS–air surface. The stronger stabilizing force is due to the larger surface tension at polymer–air interface compared to the polymer–polymer interface. The hydrodynamic response of the two layers is also different. To destabilize the PS–air interface, the viscous flow is required only in the PS layer. A deformation of the PS–PMMA interface implies however a hydrodynamic response in both polymer layers. Therefore, the PS–PMMA instability has a much larger value of \( \tau \) (several days for our experimental parameters) compared to the free surface, which destabilizes after a few hours \([4]\). Consequently, during the initial phase of the film instability, the PS layer is destabilized by the electric field, whereas the instabilities at polymer–polymer interfaces are strongly damped and the PMMA film remains essentially flat.

The initial undulations of the PS–air surface grow to form columns that span the two electrodes. During the PS column formation process, a PS/PMMA/Air contact line is formed, which moves laterally during the transition from the undulatory to the columnar phase. Because the lateral movement of the contact line generates high viscous stresses, the column formation process is accompanied by a local deformation of the lower PMMA layer at the contact line. This situation, illustrated in Fig.(6.3b) is similar to the dewetting of PS on PMMA \([6, 7]\). The local deformation of PMMA should, however, be larger in our case, due to an increased acceleration of the PS by the electric field.

Once the PS columns are formed and the PMMA substrate was exposed to air, a less damped instability (with a much lower time constant) of the PMMA surface is possible. The instability is nucleated at the locations where the electrostatic pressure is highest. This is the case at the peaks of the PMMA cusps which are adjacent to the PS columns, where the destabilizing driving
force is largest. As a consequence, the electrostatic force leads to an increase in PMMA cusp height, that is, the PMMA is drawn upward along the perimeter of the PS columns. The final morphology consists of PS columns coated by a layer of PMMA (Fig. 6.3d). We expect a thin layer of PMMA to cover the entire substrate, because PMMA wets the silicon substrate better than PS. However, this film is not favorable in terms of its electrostatic energy and its equilibrium thickness is dictated by the balance of the free energy that favors wetting and the electrostatic energy.

The reduction in structure size is given in terms of a volume conservation argument. Per unit area $\lambda^2$ the volumes of the primary and secondary structures are given by $\lambda^2 h = C V_{PS}$ and $\lambda^2 H = C V_{PMMA}$, respectively, where $h$ and $H$ are the initial layer thicknesses (see Fig. 6.3), $V_{PS}$ and $V_{PMMA}$ are the volumes of the final structures (columns) and $C$ is a numerical constant corresponding to the number of columns per unit area $\lambda^2$. For the cylindrical morphology in Fig. (6.4), $V_{PS} = \pi r^2 d$ and $V_{PMMA} = \pi (R^2 - r^2) d$ with $r$ and $R$ the radii of the PS and the composite (PS+PMMA) columns, respectively. From these simple equations, the reduction in lateral structure size is readily calculated:

$$\frac{R - r}{r} = \sqrt{1 + \frac{H}{h} - 1}$$

This argument is valid only in the absence of the PMMA layer between the columns. In our case, because the system did not reach its equilibrium, not all PMMA was drawn into the structures. Therefore, because of the presence of a laterally homogeneous PMMA layer (Fig. 6.4), $H$ must be replaced by $H_i - H_f$ where $i$ and $f$ refer to the initial and the final averaged PMMA film thickness, respectively. The reduction factor of $(R - r)/r \approx 0.12$, derived from Fig. (6.4) corresponds to a remaining PMMA film thickness of $H_f \approx 12.5$ nm.

The sample morphology formed in an electric field is far from its field–free thermodynamic equilibrium. This applies both to the PS columns and the PMMA surrounding structures. Except for very small aspect ratios, columns are not thermodynamically stable and are expected to decay via a Rayleigh instability in the absence of an applied electric field. Once formed, the columns continue growing by drawing material from the surrounding polymer layer. However, the lateral coarsening of the columnar morphology is suppressed if the columns are not connected by the laterally homogeneous film [2]. In
addition, a PMMA layer that covers the PS–air interface is unfavorable, since PS has a slightly lower surface energy and is known to segregate to the air surface.

Once the destabilization mechanism is understood, the hierarchical structure formation can be tailored [2]. Fig. (6.5) shows results where the planar top electrode was replaced by a topographically patterned silicon wafer (schematically shown in the inset). Here, the variation in the plate spacing $d$ causes a lateral variation in the electric field. Such an inhomogeneous field has two consequences. First, the capillary instability is focused toward the regions of highest electric field, i.e. toward regions where $d - (H + h)$ is smallest. The liquid polymer is drawn toward the downward extending protrusions of the top plate. Second, the characteristic time constant $\tau$ associated with the capillary instability is short in regions of small air–layer thickness. Eqn. (2.48) shows that $\tau$ decreases strongly with decreasing electrode spacing $d$ ($\tau \approx d^{-6}$ corresponding to an increase in the electric field $\tau \approx E^6$), causing a significantly earlier onset of the instability beneath the protrusions of the patterned electrode. This leads to a replication of the $1 \mu$m–wide lines in Fig. (6.5).

In Fig. (6.5b), a higher magnification AFM image of the transferred line pattern is shown. After disassembly of the capacitor device, a perfect replica-
tion of the master electrode is revealed, similar to the case of a single polymer layer \[2\]. After removing the PS by washing the sample in cyclohexane, the PMMA structures are revealed. The secondary instability generated 100 nm wide and 160 nm high structures at the edges of the replicated lines (Fig. 6.5c). The hierarchic structuring process can be explained in a similar way as the planar electrode case. The PS–air surface is destabilized initially and the PS is drawn toward the downward protruding lines, thereby replicating the master electrode. The PS line formation \((i)\) produces free PMMA surface areas and \((ii)\) causes a viscous deformation of the PS/PMMA/air contact line. The secondary instability of the PMMA–air interfaces causes a flow of PMMA to cover the PS lines.

The height and width of the PMMA structures (and therefore their aspect ratio: height/width) are determined by the electrode spacing \(d\), the lateral density of topographic features on the master wafer, and the initial film thickness of the PMMA layer. Because the PMMA is redistributed from a film into lateral structures spanning the electrodes, the width of these structures is determined by a volume conservation argument. Similar to the discussion above, \((R-r)/r = (H_i - H_f)/h \approx 0.1\), where \(r\) and \(R\) correspond to the half–width of the PS and PS–PMMA composite lines, respectively. Both our experimental results and the volume–conservation argument imply that the aspect ratio of the PMMA lines can be adjusted by varying either the thickness of the initial PMMA layer or the annealing time.

In practice, we found that achieving the final state (Fig. 6.3d) occurred only after very long times (for our experimental system, equilibration was not achieved even after several days). The time needed for the structures to develop can be significantly reduced by decreasing the molecular weight (and thereby the viscosity) of the PMMA layer. A second approach is to increase the electric field, with the occurrence of dielectric break–down of the polymer as a limiting factor. Fig. (6.6) shows a linear vertical growth of PMMA structures (all annealed at an applied voltage of 50 V for 18 hours at 170°C) as a function of the electric field. A third approach to achieve the final state shown in Fig. (6.3d) would be to increase the temperature. However, the working temperature (170°C) is already close to the degradation temperature of the polymers in air (\(\approx 210^\circ\)C) therefore, vacuum should be applied.

Finally, the reliability of this structure replication technique must be emphasized. A structured 200 × 200 μm\(^2\) area is shown in Fig. (6.7). Apart from
Figure 6.7: Large-area images of replicated patterns. To illustrate the fidelity of the replication process, optical micrographs of a $200 \times 200 \mu m^2$ replicated area are shown. The area consists of spherical cylinders arranged on a square lattice, with cylinders at each vertex and in the middle of the lines connecting the vertices. The image in a) taken immediately after the disassembly of the capacitor, shows a replicated film containing both PS and PMMA. After the removal of PS, an ordered array of PMMA rings remains on the substrate b). The magnified image in c) was obtained using dark-field illumination to enhance the optical contrast. In d) an AFM cross-section of one of the PMMA rims is shown.
isolated defects (caused by dust), the pattern of the master electrode was reproduced with high fidelity. Washing away the PS, a similar quality of the PMMA secondary structure was found. With properly aligned electrodes, structure replication can therefore be extended to very large areas.

6.4 Conclusion

In summary, a novel electric field–induced structure formation process in polymer bilayers is described. Structure formation occurs by the sequential growth of electrohydrodynamic instabilities that result in the formation of hierarchal patterns with two independent characteristic lateral dimensions. In particular, the secondary instability leads to structure widths that can be significantly smaller (by about a factor of 10) than the primary structure size. When combined with a topographically patterned electrode, this strategy can be used to replicate \( \sim 100 \) nm size structures, much smaller than the pattern size of the master. Two materials can be patterned in a one-step procedure, instead of a multi-step process used by other lithographic techniques. This approach can be extended to lateral hierarchical structures consisting of a larger number of different materials and more than two independent lateral length scales.
Bibliography

[1] Presented in the chapter regarding “Capillary Instabilities by Thermal Fluctuations”


