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Title:

***Thermocapillary Lithographic Patterning of Nanoscale Polymer Films:
Analysis, Control and Application***

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Thermocapillary Lithographic Patterning of Nanoscale Polymer Films: Analysis, Control and Applications

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Conventional photolithographic patterning of semiconductor devices relies on optical projection techniques in which the resolution limit set by the Rayleigh diffraction criterion is $O(100 \text{ nm})$. This technique, based on step-and-repeat processing of photoresist layers to create 3D-structures layer by layer, is suited to the most demanding electronic applications. There is great interest, however, in seeking less costly, lower resolution patterning methods, which are truly 3D and compatible with flat or curved substrates, for the manufacture of polymeric electronic and optical components. In this talk, we present a novel method for large-area, non-contact patterning of nanoscale films based on active thermal modulation of the polymer melt surface tension. Both passive and active modulation of the surface temperature is used to enforce and control interfacial thermocapillary stresses for molding nanoscale films into complex 3D structures whose shape is then affixed when rapidly cooled. We anticipate that nanostructures fabricated in such non-contact fashion from the molten state will exhibit superior performance due to the specularly smooth surfaces obtained upon solidification, minimizing the scattering losses.

This method of 3D patterning on demand arose from careful re-examination of experiments conducted by several groups during the past decade [1–3] in which it was reported that a nanoscale molten film subject to an ultra large transverse gradient undergoes spontaneous formation of self-assembling nanopillar arrays with mean pillar spacing λ_{\max} . In such experiments, a film of molten polymer like PS or PMMA, ranging in thickness from $80 \text{ nm} \lesssim h_o \lesssim 130 \text{ nm}$, is placed on a flat substrate at temperature T_2 ranging from $130^\circ\text{C} - 170^\circ\text{C}$. This substrate is then overlay by a second cooler one at temperature T_1 such that a small air gap of thickness $d_o - h_o$ is maintained above the polymer film. Vertical spacers are used to maintain a total separation distance of $100 \text{ nm} \lesssim d_o \lesssim 600 \text{ nm}$. The free surface of the polymer film is therefore cooled from above by proximity to the cooler substrate. During the formation process, all temperatures are maintained above the polymer glass transition to ensure the film remains in a molten state. Despite that the overall

temperature difference $10^\circ\text{C} \lesssim T_2 - T_1 \lesssim 55^\circ\text{C}$ is not large, the small gap size establishes an ultra large transverse gradient $\Delta T/d \sim 10^6 - 10^8 \text{ }^\circ\text{C}/\text{cm}$. After heating overnight, the system is then quenched to room temperature to solidify the structures formed.

It is currently believed that a radiation pressure caused by internal reflection of thermal acoustic phonons (AP) within the tight confines of a nanoscale film generates a destabilizing normal force that exceeds the stabilizing force of capillarity [4, 5]. According to this model, undulations in the film thickness cause spatial modulation of the local phonon density and acoustic pressure such that protrusions develop into elongated pillars which grow toward the upper plate while depressions advance toward the lower one. We will discuss the shortcomings of this model and demonstrate instead by linear stability analysis and finite element simulations of the corresponding non-linear interface equation that thermocapillary stresses caused by a temperature dependent surface tension play a crucial and even dominant role in the patterning process. Direct comparison of the functional dependence of λ_{\max} with d_o for various values of h_o , ΔT , and other material parameters with actual measurements of the mean pillar spacing yields very good agreement using no adjustable parameters. However, the experimental input values of h_o lead to a systematic over estimate of λ_{\max} by as much as 35% - 40%. Careful evaluation of experimental conditions has revealed that this discrepancy is likely due to use of spun cast films that were not annealed prior to insertion in the experimental assembly. The reported values for h_o represent the thickness of swollen polymer films, which undergo shrinkage from solvent evaporation after placement on the hot substrate. An additional source of discrepancy may also be due to the fact that the confining substrates in the experiment are slightly tilted in order to access various values of d_o within one setup. Such a tilt can cause capillary migration of the pillars toward narrower gap width and subsequent smaller measured values of λ_{\max} .

In support of studies to further use of thermocapillary actuation for lithographic applications, we have extended our simulations to systems in which the upper substrate is pre-patterned with complex geometrical shapes. These topological variations generate distinct thermal surface profiles which are mapped by conduction onto the polymer/air interface. For feature sizes smaller than λ_{\max} , we can bypass the evolution of the natural hydrodynamic in-

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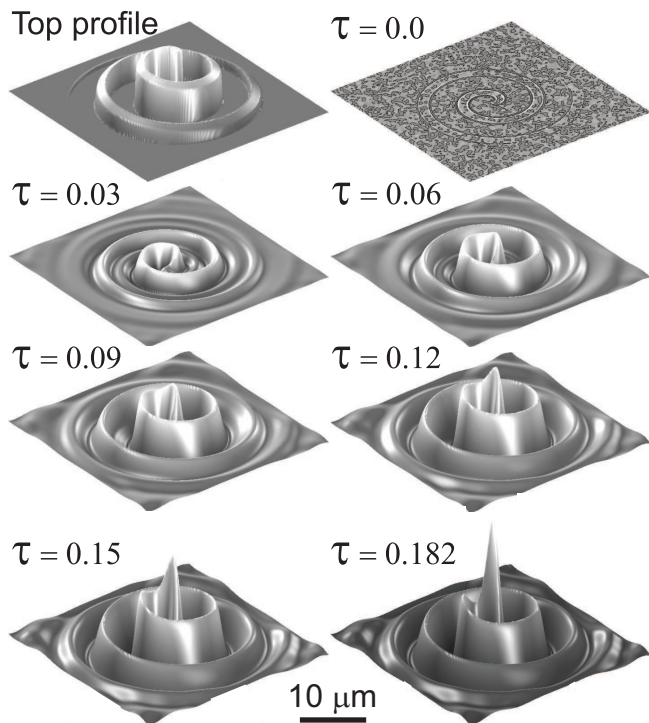


FIG. 1: Snapshots of the thin film evolution in time if the upper substrate has a topology according to the Archimedean spiral (shown in the upper left image, 'Top profile') for $h_o = 100$ nm, $\Delta T = 46$ K, $d_o = 285$ nm and the peak of the Archimedean spiral at the center with $\Delta d_o = 0.4h_o$. The computational domain length in each lateral direction in these images is $\approx 29 \mu\text{m}$. The peak values in the film thickness at the center are: $\tau=0.0$: $h/h_o - 1 = 2 \cdot 10^{-4}$. $\tau=0.03$: $h/h_o = 1.084$. $\tau=0.06$: $h/h_o = 1.159$. $\tau=0.09$: $h/h_o = 1.262$. $\tau=0.12$: $h/h_o = 1.419$. $\tau=0.15$: $h/h_o = 1.695$. $\tau=0.182$: $h/h_o = 2.423$. $\tau=1$ corresponds to 2.3 hrs.

stability and impose thermocapillary stresses which trigger a mirror image of the substrate topology onto the polymer film to achieve excellent fidelity upon replication. In Fig. 1 is shown an example of such replication for a height-varying Archimedean spiral based on

finite element simulations which couple thermal conduction across an air/polymer bilayer to the interfacial thermocapillary stresses driving the film deformation. The top left image shows the inverted topology defined along the upper substrate which should be reproduced in the film. The other images show snapshots in time of the film interface deformation process. Feature reproduction is quite good for early times, especially given that the 3D structure is shaped in one step, unlike fabrication by conventional lithography. Non-linear effects and thermocapillary waves established near sharp edges become significant for late times, causing feature blurring. We discuss how these effects can be minimized to enhance pattern fidelity by the optimization of geometries, operating conditions, material properties as well as process timing for attaining minimal pitch and feature size. In future work, we are exploring temporal modulation of this non-contact patterning technique for "active TC lithography" of 3D structures in which site-specific thermal gradients and plate separation distances can be digitally tuned for selective growth of protrusions or depressions of flat or curved films.

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