# Observation of dynamic behavior of lithographically induced self-assembly of supramolecular periodic pillar arrays in a homopolymer film

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The dynamic behavior of lithographically induced self-assembly (LISA), a newly discovered pattern formation phenomenon, was recorded and analyzed with real time video. Two surprising and intriguing phenomena were observed. First, a LISA pillar array was formed in an orderly manner starting under the corners of a mask pattern, then the edges, and later propagating to the center of the mask pattern. Second, the time interval between the formation of two subsequent LISA pillars has a shell structure. The observation presents evidence critical to uncovering the physical origin of this phenomenon, which is believed to be related to the interplay of electrodynamics, fluid hydrodynamics, and polymer chemistry at the nanometer scale. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1398616]

Lithographically induced self-assembly (LISA), a newly discovered pattern formation phenomenon occurring at the micron or submicron length scale, offers a unique and important method for patterning polymer electronic and optoelectronic devices without the use of photoresist, exposure, and developer.[1,2] In LISA, a plate (called mask), placed a distance above a viscous, thin homopolymer film, causes the polymer film, initially flat on another plate, to self-assemble into periodic pillar arrays[1] [Fig. 1(a)]. The pillars, which grow in opposition to the surface tension of the polymer melt, bridge the two plates and have a height equal to the plate–mask separation. If the mask surface has a protruding pattern or a surfactant pattern (in the shape of a triangle or rectangle, etc.), a LISA pillar array is observed to form only under the pattern. Its boundary is aligned to the boundary of the mask pattern and its lattice structure is determined by the geometry of the mask pattern. It has been shown[2] that LISA is not caused by a Rayleigh–Benard instability[3–5] nor by surface tension driven Benard instabilities[5–7] because the film in our experiments is so thin. The Rayleigh and Maragoni numbers are orders of magnitude below the critical values needed for such instabilities. LISA is not related to the phase separation of polymer blends[8] or di-block copolymers[9] since only a single homopolymer is used. LISA is also different from other pattern formation processes in chemistry and biology[5,10,11] since there is no chemical reaction taking place. The image charge induced (ICE) model was proposed which identified the electrostatic force as the driving force for LISA.[2] Pattern formation is thought to occur as a result of the interplay between the electrostatic force and the hydrodynamic forces in the polymer melt, but the exact reason for the periodicity of the LISA pattern is still an open question. Furthermore, the exact sources of the electrostatic force need to be clarified. To answer these questions, an understanding of the dynamic behavior of the LISA process becomes crucial.

We report the observation of the time evolution of LISA pattern formation. It reveals that LISA pillar arrays are formed in an orderly manner: one pillar at a time, starting under the corners of a mask pattern, then the edges, and later propagating to the center of the mask pattern. Furthermore, the time interval between the formation of subsequent pillars shows a well-defined structure. In order to monitor the pattern formation process of LISA in a polymer film, the LISA mask was made of quartz, thus allowing for observation through the mask using an optical microscope. The evolution of the pattern was recorded by a CCD camera and tape recorder with a time resolution of 30 ms [Fig. 1(b)]. The polymer used in our experiment was polymethyl methacrylate (PMMA) with a molecular weight of 2000 Da (2 K) and glass transition temperature of 96 °C. A solution of PMMA dissolved in chlorobenzene was spin coated onto a silicon substrate. The mask was patterned with a fluorinated silane surfactant using standard photolithography.

The LISA sample and mask were separated by a spacer and were held together by a metal chuck. The spacer consisted of an array of 220 nm high aluminum lines deposited

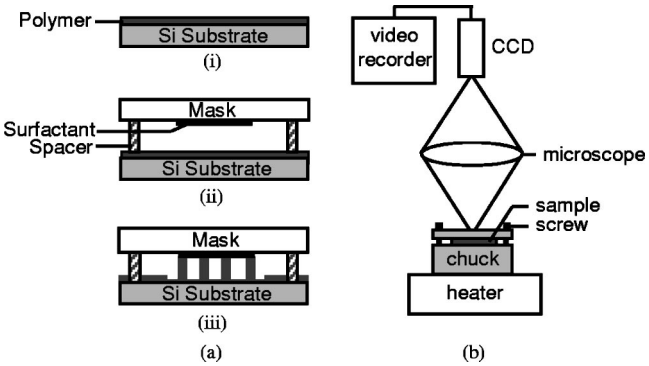


FIG. 1. (a) Schematic of lithographically induced self-assembly (LISA): (i) thin layer of homopolymer cast on a flat silicon wafer; (ii) mask of surfactant patterns placed a distance above the PMMA film, but separated by a spacer; (iii) during a heat-and-cool cycle, the polymer film self-assembled into a periodic supramolecular pillar array, with the location and lattice structure of the array controlled by the boundary and geometry of the mask pattern; (b) schematic of the experimental setup.

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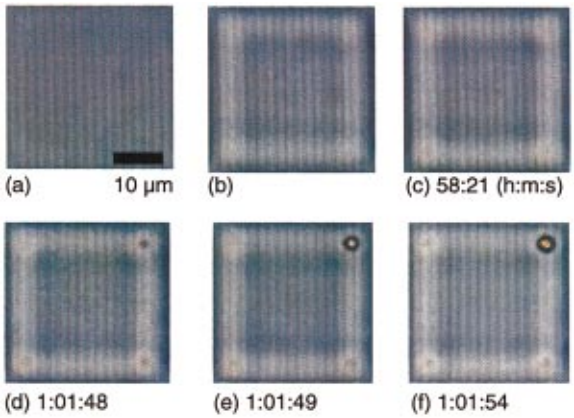


FIG. 2. (Color) Observed dynamic behavior of the growth of the first pillar of a LISA array under a square mask pattern at 120 °C. (a) Polymer was featureless before heating the system; (b) once the system reaches 120 °C, a latent image of the pattern can be seen. This was taken as the reference for the times. (c) Corners become more prominent than the perimeter; (d) first pillar just touches the mask and (e)–(f) expands to its final size.

on the mask by electron beam evaporation through a shadow mask. The entire sample assembly was heated on a hot plate. The temperature was monitored by a thermocouple and deviated by less than 2 °C across the sample.

The dynamic behavior of a LISA pillar array forming under a square mask pattern is summarized in Figs. 2 and 3. The PMMA film was originally 135 nm thick. Figure 2 shows the growth of the first pillar in the array. Note that the color and contrast of the images have been enhanced for clarity. We heated the sample from room temperature to 120 °C and maintained that temperature for the remainder of the experiment. Before heating the system, the PMMA was featureless [Fig. 2(a)]. The temperature was increased at a rate of ~10 °C/min up to 100 °C and then at 1 °C/min after. Once the temperature exceeded 110 °C, a very faint image showing the outline of a pattern could be observed and was clearly visible once the system reached 120 °C [Fig. 2(b)]. The onset of 120 °C was chosen as the zero time reference in Fig. 2. The latent pattern indicates the start of pattern formation and is visible because the polymer in that region is several tens of nanometers higher than the surrounding film. It took about one hour for the first pillar to reach the mask, at which point it appeared as a black point in the center of a bright circle [Fig. 2(d)], and then expanded into a 5 $\mu$m diameter dot in 6 s [Figs. 2(e) and 2(f)]. This suggests that pillars first grow as a cone-shaped spike in the polymer film and then, after touching the mask, reshape into pillars with a flat top and vertical sidewalls. The amount of spreading of the polymer on the mask surface was limited due to the low surface energy of the surfactant used in patterning the mask.

Figure 3 shows the growth behavior from the first pillar to the last pillar of a LISA array formed under a square mask pattern. The time zero in this figure is set at the completion of the first pillar. The second pillar formed 9 s after the first pillar in a corner of the pattern adjacent to the first pillar [Fig. 3(b)]. The remaining corners followed soon thereafter. After the pillars at the corners were completed, new pillars started to form at the edges of the mask pattern [Figs. 3(e)–3(g)]. A new edge pillar was always observed to form adjacent to an existing pillar.

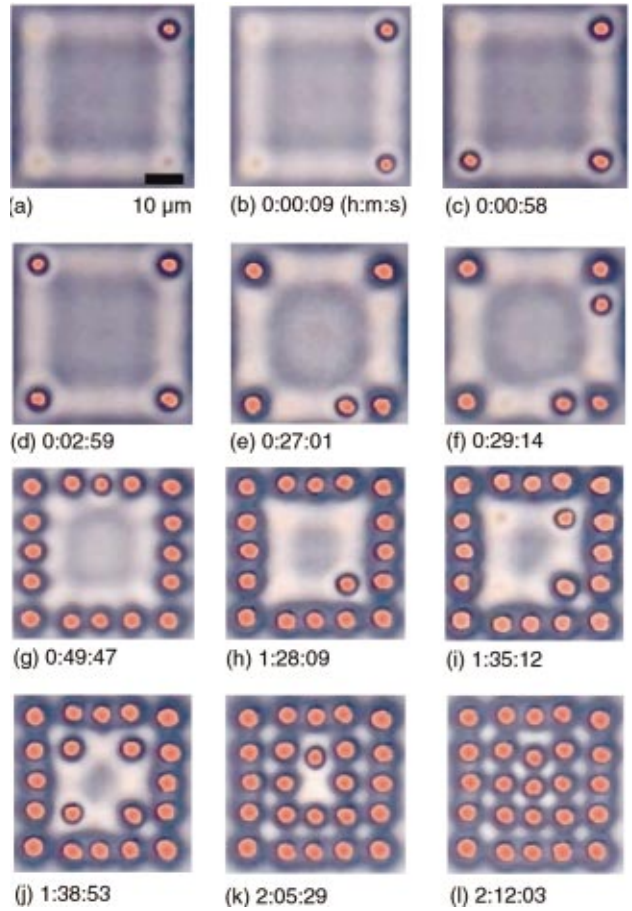


FIG. 3. (Color) Observed dynamic behavior of the growth of a LISA array formed under the square mask pattern at 120 °C from the first pillar to the last pillar. The pillars were formed in an orderly manner, first under the corners of the mask pattern, then along the edges. The interior of the pattern forms in a similar fashion. The completion of the first pillar was set as time zero.

50 min after formation of the first pillar, the perimeter of the array is fully formed and a latent image of the inner pillars can be seen [Fig. 3(g)]. In a fashion similar to the formation of the perimeter, a new pillar was formed first in a corner, then adjacent corners, and later along the edges [Figs. 3(h)–3(k)]. Similar dynamic behavior has been observed in square patterns with different sizes as well as with mask pattern having different shapes (e.g., triangles and rectangles).

Following completion of the LISA pattern, the system

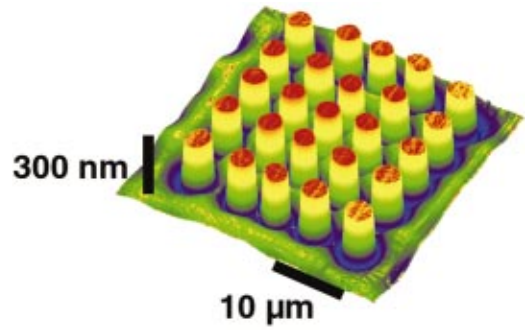


FIG. 4. (Color) Atomic force image of the same LISA pillar array (5×5 pillars) as in Figs. 2 and 3. The pillars are flat on top and have a height, diameter, and period of 310 nm, 5 $\mu$m, and 9 $\mu$m, respectively. The array has a simple cubic lattice.

was allowed to cool in air to room temperature thus fixing the patterns that had formed. After removal of the mask, the LISA sample was examined by atomic force microscopy (AFM). Figure 4 shows the AFM image of the same LISA array pattern shown in Figs. 2 and 3. The image shows that the diameter of each pillar is uniform and that the top of each pillar is flat. The pillar height, diameter, and period are 310 nm, 5 $\mu$m, and 9 $\mu$m, respectively. The measured height suggests that the actual mask-substrate spacing was 310 nm and that the aluminum spacer was pressed 45 nm into the PMMA.

The time sequence is summarized in Fig. 5 and shows pillar formation as a function of time [Fig. 5(a)] and the time interval between subsequent pillars [Fig. 5(b)]. The plots show a shell structure in the formation process. After completion of the corners, a long time is required ($\sim$26 min) to form the first edge pillar. Another delay is observed before the formation of first inner pillar. Within each shell, however, the average time interval is relatively short.

The total time for a complete LISA process in a 135 nm thick 2 K PMMA film with a 175 nm mask-polymer separation at 120 °C is more than 2 h. This time is measured after the appearance of the first pillar, which itself took about 1 h to form. Further experiments were performed to characterize the rate of formation as a function of the initial separation between the mask and polymer. Qualitatively, the rate was observed to decrease with increased separation; however, a clear trend was not discernible due to large variability in the data. Similar variability was encountered in assessing the effect of the PMMA film thickness. It is likely that such measurements are limited by the experimental setup. In our system, it is unclear how far the mask spacers have been forced into the polymer melt until after the pattern has formed and the mask removed. This makes it difficult to differentiate between the effects of film thickness and the effects of the separation between the mask and polymer surface.

Based on the above observations and other experimental data, a better model of LISA has been developed that couples the electrical force to the surface tension and elasticity of the polymer.[12] From the model it is apparent that the polymer film under a protruding mask pattern experiences a stronger electrostatic interaction with the mask than does the surrounding region of polymer. The interaction leads to a reduced pressure in the polymer under the mask, giving a pressure gradient that drives the surrounding polymer towards the region underneath the mask pattern. Since the corners experience the largest lateral pressure gradient, pillars should grow there first, as is seen in our experiment. In general, the four corner pillars do not form at exactly the same time because the flow of polymer is not symmetric. It is influenced by the proximity of other LISA patterns and by nonuniformities in the polymer or mask surface.

The polymer under the edges of the mask pattern experiences a pressure gradient in only one direction leading to a small accumulation of polymer around the perimeter of the pattern. The corner pillars and the polymer crest along the edges serve as boundaries for the formation of subsequent pillars. Further details of the model and simulation results will be presented elsewhere.[12]

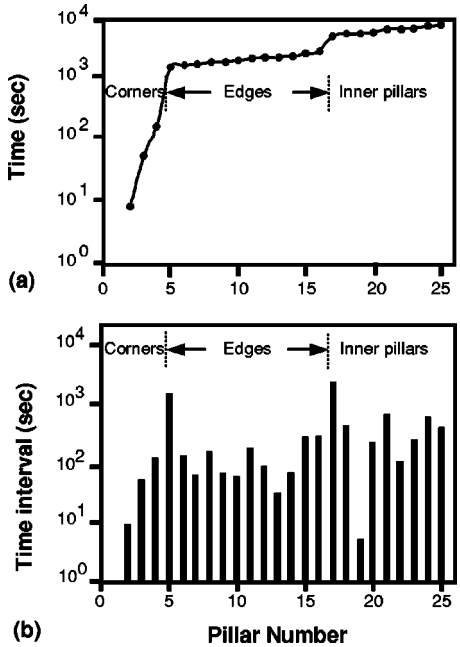


FIG. 5. (a) Time evolution of pillar formation as a function of pillar number; and (b) the time interval between formation of one pillar and the previous one as a function of pillar number. The zero reference time is set at the completion of the first pillar. The time interval exhibits a shell structure: a long time is required between the corner pillars and the edge pillars, and between the edge pillars and the inner pillars.

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