High Aspect Ratio Pillar Arrays Formed via Electrohydrodynamic Instabilities

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Directed-assembly based patterning techniques are appealing because of their ability to harness natural phenomena to form useful structures. Recently, a technique has emerged that is capable of forming ordered polymeric pillar arrays.[1-6] Pillars are formed by the amplification of thin film surface instabilities through the application of an electric field normal to the film surface. Experimentally this is achieved by placing a thin film coated substrate within planar proximity of another surface, forming a simple capacitor. Applying an electric field across the gap results in the formation of an array of uniformly sized pillars. Pillars form due to the force imbalance at the film interface where the electric field amplifies film undulations against the restoring forces of gravity and surface tension. Features as small as 140 nm have been created using this method through the use of templates with relief patterns.[1]

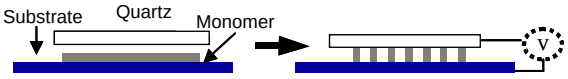

Figure 1. The pillar array formation process: An electric field is applied across a thin monomer film, with a bias (V). The electric field amplifies film undulations, resulting in pillars, which are then photocured through the transparent quartz template.

The dynamics of pillar formation have been modeled using 3-D non-linear simulations[7] and linear stability analysis, which describes the initial amplification of film undulations.[1,3,8-12] The intermediate growth of pillars is usually explained as slowly growing undulations that eventually span the capacitor gap. Our experimental observations show that this proposed mechanism is incomplete. We have observed the formation of small fibrils that emanate from the undulations and project across the gap to initiate the pillar growth process. These polymeric fibrils have very high aspect ratios and can be used to form novel 3-D cage type structures through the use of a bi-layer film stack (e.g. PS on PMMA).

In a parallel effort to create high aspect ratio pillar arrays, we have developed a sophisticated tool capable of stretching pillars and controlling the key physical parameters in pillar formation (i.e. gap size and e-field strength). In the absence of stretching, the pillar structures reported to date have had low aspect ratios (less than unity).[10] Here we will show that the aspect ratio of these structures can be uniformly increased by stretching. The tool utilizes three servo motors to manipulate the positioning of the upper electrode of the capacitor device and the resulting gap is measured using white light interferometry. The systematic control provided by this tool allows the study of the effects of geometry on pillar formation dynamics.

Traditionally, high Tg polymer films have been used to form pillar arrays. These materials require a heating step to induce flow prior to pillar formation and a cooling step to lock the columnar structures into place after formation. This time intensive heating cycle is eliminated through the use of low viscosity photocurable monomers, which form pillars rapidly at room temperature. Use of these materials reduces the processing time from hours to seconds due to the lowered film viscosity and the elimination of the heating / cooling cycle required for polymers. The pillar structures are locked into place by irradiating the photocurable solution through a transparent template.

We have identified several material systems that are ideal for pillar formation. Thiol-ene systems seem to be the most promising materials for pillar arrays due to their insensitivity to atmospheric species and their unique radical step polymerization mechanism, which permits control of certain material properties as a function of conversion. These materials form pillars nearly instantaneously under relatively small electric fields (2 V/um) and rapidly cure under ambient conditions. Figure 2 shows an optical micrograph of a silicon substrate covered with thiol-ene pillars with a characteristic spacing of ~40 μm. The structures in Figure 2 are composed of a 1:1 molar mixture of a thiol component, pentaerythritol tetrakis 3-mercaptopropionate (Aldrich 381462), and a vinyl ether component, tris [4-(vinyloxy)butyl] trimellitate (Aldrich 49,650-2). This formulation is particularly desirable because it photopolymerizes in the absence of a traditional initiator. The pillars in Figure 2 were formed and cured within seconds.

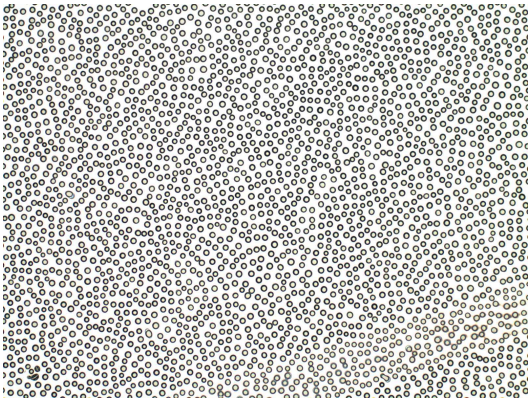

Figure 2. Optical micrograph of photocured thiol-ene pillars on a Si substrate.

These thiol-ene materials and others were studied using the active gap tool. Results demonstrate nearly an order of magnitude increase in aspect ratio accomplished via stretching.

References:

(1) Schaffer, E.; Thurn-Albrecht, T.; Russell, T. P.; Steiner, U. *Nature (London)* **2000**, *403*, 874-877.

(2) Chou, S. Y.; Zhuang, L. *Journal of Vacuum Science & Technology, B: Microelectronics and Nanometer Structures* **1999**, *17*, 3197-3202.

(3) Schaffer, E.; Thurn-Albrecht, T.; Russell, T. P.; Steiner, U. *Europhysics Letters* **2001**, *53*, 518-524.
(4) Lin, Z.; Kerle, T.; Baker, S. M.; Hoagland, D. A.; Schaffer, E.; Steiner, U.; Russell, T. P. *Journal of Chemical Physics* **2001**, *114*, 2377-2381.
(5) Chou, S. Y.; Zhuang, L.; Deshpande, P.; Chen, L.; Sun, X. *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **2000**, *41*, 78.
(6) Schaffer, E.; Harkema, S.; Roerdink, M.; Blossey, R.; Steiner, U. *Advanced Materials (Weinheim, Germany)* **2003**, *15*, 514-517.
(7) Verma, R.; Sharma, A.; Kargupta, K.; Bhaumik, J. *Langmuir* **2005**, *21*, 3710-3721.
(8) Herminghaus, S. *Physical Review Letters* **1999**, *83*, 2359-2361.
(9) Pease, L. F.; Russel, W. B. *Journal of Chemical Physics* **2003**, *118*, 3790-3803.
(10) Pease, L. F., III; Russel, W. B. *Langmuir* **2004**, *20*, 795-804.
(11) Lin, Z.; Kerle, T.; Russell, T. P.; Schaeffer, E.; Steiner, U. *Macromolecules* **2002**, *35*, 3971-3976.
(12) Pease, L. F.; Russel, W. B. *Journal of Non-Newtonian Fluid Mechanics* **2002**, *102*, 233-250.