

Electrically Induced Pillar Arrays Formed Using Photocurable Materials

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Interest in alternative patterning techniques has grown as the resolution of traditional photolithography begins to approach fundamental limits. In general, self-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 massively parallel, 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, as seen in Figure 1. 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

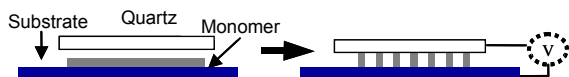


Figure 1. The pillar array formation process: An electric field is applied across a thin monomer film, with a bias (V). The electric field amplifies film undulations, resulting in pillars, which are then photocured through the transparent quartz template.

To date, this process has only been performed on polymer films, which require a heating step to induce flow prior to pillar formation and a cooling step to lock the columnar structures into place after formation. Here we show that this process can be performed using photocurable monomers at room temperature. This 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.

Materials for the pillar formation process must be tailored to meet several processing requirements. First, the material must photocure rapidly to high conversions under ambient conditions. The throughput of the process is impacted by the cure rate while the mechanical stability depends both on the extent of polymerization and the degree of crosslinking. When the template is removed, the photocured polymer must adhere entirely to the substrate and maintain structural integrity. In addition, the monomer solution must form a stable film on a substrate, which involves considerations of both surface energy and volatility.

There are a number of material classes such as acrylates, vinyl ethers, and thiol-enes that meet the requirements for the pillar formation process. Acrylates and vinyl ethers rapidly form pillars, but are inhibited by ambient species such as oxygen, base, and water.

Specifically, oxygen inhibits the free radical polymerization mechanism of acrylates by quenching reactive radicals. As the pillars are irradiated, photo-generated radicals consume the dissolved oxygen within the pillars. Oxygen is continually replenished in the pillar by diffusion from the ambient due to the high surface to volume ratio of the pillars. Thus, acrylate based pillars never polymerize to the point necessary to attain structural integrity. Vinyl ethers are typically cured via the oxygen insensitive cationic mechanism. Vinyl ethers are not ideal candidates for pillar formation for several reasons. The polymerization is inhibited by base and water. Additionally, there are few commercially available vinyl ethers that have low enough volatility to form stable films.

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 a scanning electron microscopy (SEM) image of a silicon substrate covered with thiol-ene pillars. 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-(vinylloxy)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.

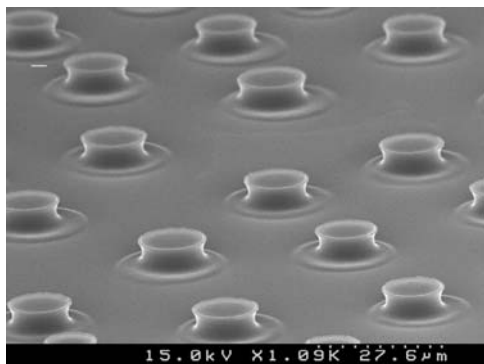


Figure 2. SEM image of a photocured thiol-ene pillars on a Si substrate. The upper electrode has been removed to allow for imaging.

The relatively low viscosity of photocurable monomeric materials enables pillar formation to occur orders of magnitude faster than traditional polymers. Thiol-ene materials are ideal for photocurable pillars because they form stable films with low viscosities and photocure rapidly under ambient conditions.

- (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.