Novel Polymer Patterns Formed by Lithographically Induced Self-Assembly (LISA)

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A variety of self-assembly patterns, e.g., concentric rings, rods, and pillars, in polymer thin film have been achieved by lithographically induced self-assembly (LISA) in this study. The variations of the LISA patterns are controlled by many operation factors, such as the choice of the polymers, mask topology, process temperatures, surface tension, and so forth. It was found that as the inter- and intramolecular hydrogen bond interactions were incorporated into the polymer [poly(methyl methacrylate-*co*-methacrylic acid)], novel LISA patterns such as rods and corresponding arrays (concentric ring, triangle, hexagonal, etc.) were formed, in addition to the pillar arrays formed in poly(methyl methacrylate) under the same experimental conditions. The origins of the rod array are determined by the topology of the masks. Under a plain mask, the patterns developed from any nonuniform defects (spots) on the mask or polymer thin film and propagated outward. However, under a mask with protruding flat patterns, the rod patterns started along the edge of the protrusions and propagated inward. By increasing the process temperature, those novel rods and corresponding array patterns could transform back to pillar or pillar arrays.

Introduction

Lithographically induced self-assembly (LISA) is a newly discovered self-assembly phenomenon observed in polymer thin films.[1] Although the self-assembly phenomenon of macromolecules has attracted great attention and been studied extensively in recent years, most work was on amphiphilic block copolymers in solutions[2,3] and phase separation structures in multiphase polymer films.[4] Those self-assembled structures are based on the solubility or compatibility differences between the chemicals or components, which provide chemically distinct regions within the structures.

However, the formation of LISA patterns is fundamentally different from other pattern formation processes. Instead of chemical incompatibility, LISA is induced by the internal electrical field between mask and polymer surface. LISA patterns are well-defined topological patterns on the substrate at the micrometer or submicrometer length scale[1] with the same chemical composition. In a LISA experiment, a thin polymer film is spin-coated uniformly onto a substrate. Then a mask with a spacer will be mounted on top of the polymer film. A uniform pressure is required to hold the mask close to the polymer surface to form a "sandwich", leaving a gap in between, which is controlled by the polymer thickness and spacer height on the mask. The incomplete closed "sandwich" system is heated to above a certain temperature, such as Tg of the polymer thin film, to develop the LISA patterns. The formed LISA patterns are kept by cooling the system to room temperature. The driving force for LISA formation is the electrical forces generated by the image charge.[1] Schaffer et al. affirmed that the electrical force is the main driving force by simulation and external electrical field experiments.[5]

LISA offers a unique and important method for patterning electronic, optoelectric, and other devices without using traditional lithographies.[6] The periodic pillar arrays in poly(methyl methacrylate) (PMMA) thin films have been studied in detail by Chou et al.[1] The dynamic behavior of LISA pillar arrays has also been explored.[7]

In this paper, we extend our study to a polymer other than PMMA, poly(methyl methacrylate-*co*-methacrylic acid) (PMMA−MAA), and explore novel patterns, such as rod array (concentric ring, triangle, and hexagonal) structures, besides pillars. In addition, the effects of the mask and temperature on LISA pattern formation are discussed.

Experimental Section

Polymer Thin Film. PMMA−MAA (acid content 1.6%, mole ratio) (Mn = 15,000) (Aldrich) was dissolved in chlorobenzene (HPLC, Aldrich) to prepare a 2.0% (w/w) solution. The prepared solution was then spin-coated onto a silicon wafer, which had a thin layer of native oxide. The final polymer thickness was around 100 nm.

Masks. Both plain and patterned (with flat triangles, circular, and hexagonal protrusions in the range of 5−100 μm) masks were used in this study. The mask material was a 200 nm layer of thermally grown oxide. An array of the spacer was fabricated on SiO_2 by photolithography to ensure that the gap between the polymer and the mask was consistent. The spacers were 3 μm in diameter and 150 nm in height (from the foot of the spacer to the SiO_2 flat surface). The flat protrusions were made by using photolithography followed by reactive ion etching. The height of the protrusions was around 50 nm. All of the SiO_2 mask surfaces were then coated with a fluorinated alkylsilane surfactant monolayer.

LISA Process. The detailed scheme for the LISA setup is shown in Figure 1. At first, the mask with spacer was mounted

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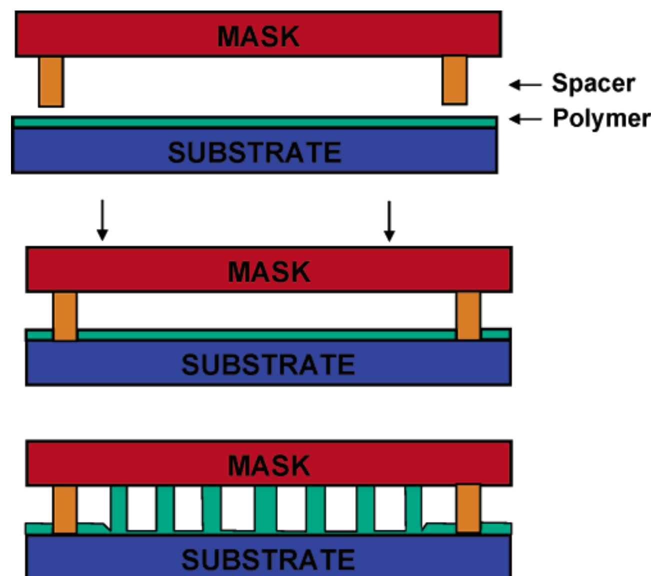

Figure 1. Scheme of the LISA experimental setup.

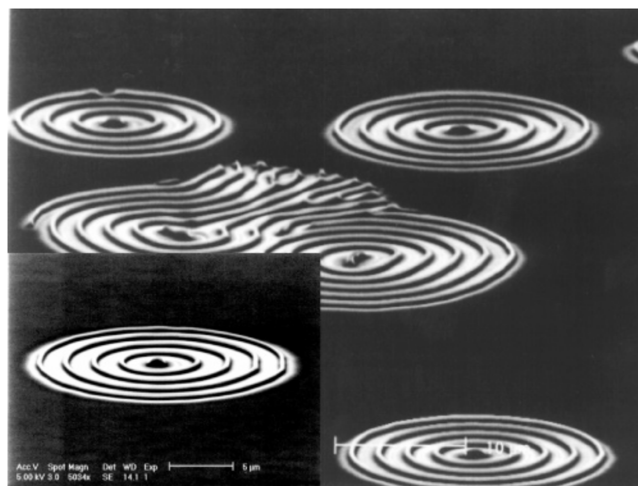

Figure 2. SEM picture of LISA patterns formed in PMMA−MAA under a plain mask.

on top of the polymer film. A 50 nm gap was maintained between the polymer and the mask surface by using spacers and 40 lb/cm^2 pressure in our experiment. Then, the mask, polymer thin film, and substrate "sandwich" were heated to 160−200 °C, which is above the Tg of PMMA−MAA (118 °C). The system was kept at that temperature for 20 min before cooling down to room temperature. Finally, the mask could be removed from the LISA pattern when it was solidified.

Characterization. The LISA patterns were monitored by a digital optical microscope (Nikon Optiphot 150 with a Diagnostic digital camera), atomic force microscope (AFM) (Digital Instruments 3100), and scanning electron microscope (SEM) (Philips XL 30 FEG). The glass transition temperature (Tg) of the polymers was obtained using a differential scanning calorimeter (DSC) (Perkin-Elmer DSC 6).

Results and Discussion

As mentioned in the Experimental Section, in this study 1.6 mol % carboxylic acid groups are incorporated along polymer chains. The incorporation of carboxylic acid side chains imparts strong inter- or intramacromolecular hydrogen bond interactions inside the polymer thin film. The existence of the hydrogen bonds makes the movement of PMMA−MAA chains more difficult than that of PMMA having the same molecular weight. DSC analysis proved that the Tg for PMMA−MAA (118 °C) is higher than that of PMMA (105 °C).

As the flow ability of the polymer was reduced, novel concentric rings, spirals, or rodlike patterns were formed in the PMMA−MAA thin film. A SEM picture (Figure 2) shows that the width of each line is 400 nm and the space between neighboring lines is around 1.6 μm. The diameter of the central pillar is 1.6 μm, and the radii of the rings are 3.3, 5.3, 7.3, and 9.3 μm, respectively.

Although self-assembled concentric rings and rodlike patterns also have been found in a fluid undergoing Rayleigh−Benard convection for a long time,[8] LISA is not due to the instabilities from the thermal convection; it is a mask-based pattern formation procedure. Actually none of the current theory is suitable to explain the origin of LISA patterns. A new model, called the image charge-induced electrohydrodynamic-instability (ICE) model, has been proposed by Chou[9] to explain the LISA phenomenon (Figure 3). According to that model, LISA patterns are formed as a result of the interplay and instability of charge in the polymer melt, image charge in the mask, and hydrodynamic forces in the polymer melt.[9]

As introduced, LISA is induced by the mask. Therefore the effect of the mask on the pattern formation is studied. Figure 2 shows the self-assembled concentric rings in PMMA−MAA formed under a plain mask. For a plain mask, the seed for forming a ring is due to the nonuniformity in the topology of the PMMA−MAA thin film or mask surface. According to the ICE model,[9] any defect dot in the topology will result in charge accumulation in certain regions thus giving a nonuniform charge distribution. Therefore the electrostatic force between the polymer and the mask is stronger in some places than in others (Figure 3a). If this interaction exceeds the surface tension and gravitational force, PMMA−MAA at that point will be pulled up to form the central pillar in concentric ring patterns. Once the central pillar is formed, the charge must redistribute. The central pillar acts like a perturbation which causes a circular capillary wave front in the polymer melt surface. Instead of forming another pillar, the capillary wave in PMMA−MAA will grow to form a ring around the central pillar. Once the first ring is formed, the process will repeat to form the other concentric rings and the process will develop from the center toward the outside.

Video observation,[7] simulation, and intentional central dot control confirmed that the polymer LISA patterns developing from a central dot under a plain mask would propagate outward.[10]

Similar concentric ring arrays can be induced by flat circular protrusions on the mask with a diameter much larger than the dots as shown in Figure 4a. However the pathways to develop those rings under circular protrusions are different from those of the rings induced by the dot in Figure 2.

For the case with a flat circular protruding pattern on the mask, the boundary plays an important role in the ring formation. It is found that the ring develops along the edge of the circle mask first. Once the boundary circle is finished, the next circle inside begins to grow inside the first one. As time goes on, the rings develop from outside to inside. These edge patterns develop because of nonuniformity in the pressure distribution in the polymer melt. The polymer under the mask feels an upward driving

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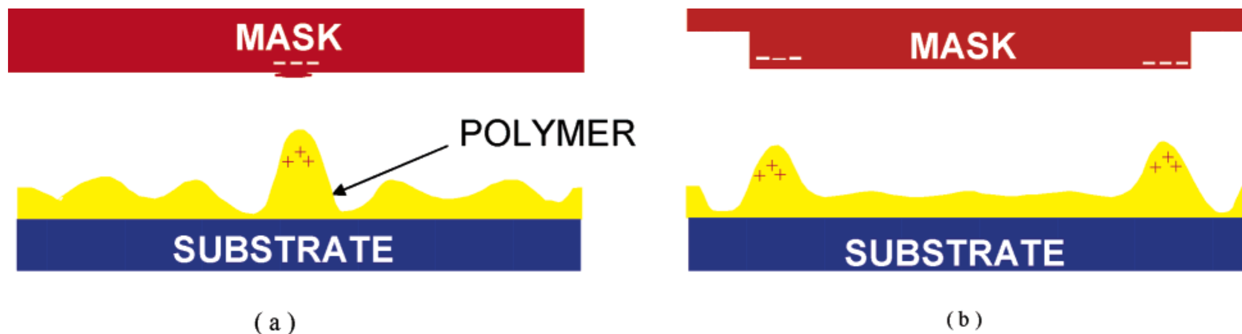

Figure 3. Schematic illustration of the origin of LISA patterns under (a) plain (ref 9) and (b) flat protruding (ref 11) masks.

Figure 4. AFM images of LISA structures: (a) concentric rings; (b) triangle array; (c) hexagonal array (on the right) and the corresponding flat protrusion masks used to induce the LISA patterns (on the left).

force which lowers the pressure in that region. Surrounding regions are at higher pressure and thus flow toward the edges of the polymer region under the protruding pattern (as shown in Figure 3b).[11] According to the ICE model, the image charges on the mask can move along the boundary and accumulate on the corner first, so the driving force for the polymer thin film under the corner of the mask is the strongest. Therefore the pattern formed under a protruding mask develops from the corner and grows along the edge.

To confirm the boundary effect of the protruding patterns on the mask, flat triangle and hexagonal protrusions were applied to form LISA patterns underneath. Figure 4b,c also shows that the patterns grow along the edges of the mask pattern first and develop from the outside to the center. For all of the structures, the line width and the space between the neighboring lines stays constant. The self-assembled lines never cross; they always form parallel to existing lines. There is almost no polymer left between the lines.

Besides the mask topology, the process temperature also affects the pattern structures. The effect of the temperature is to change the polymer thin film flow ability or polymer melt viscosity. It has been shown by Williams–Landel–Ferry (WLF) that the polymer melt viscosity decreases with increasing temperature.[12] In our experiment, as the processing temperature is raised from 170 to 200 °C, H-bond interaction inside the polymer decreases and the polymer movement ability increases. Therefore more and more polymers are sucked to the mask and the width of the lines tends to increase. Since the polymer volume is limited, when the temperature is raised to above 200 °C, those parallel lines begin to break and convert to regular pillar arrays. The diameter of the pillar (3.0 μm) is much larger than the line width of the rings or rods (400 nm). From the polymer point of view, the above result indicates that low flow ability favors formation of rods or rod arrays while high flow ability favors formation of regular pillar arrays (Figure 5). On the other hand, the surface tension difference between the polymer and the underlying substrate also plays an important role in determining the LISA structures. It is found that when we added ions inside the polymer to increase the surface tension of PMMA[10] or reduced the surface tension of the substrate underneath, PMMA also can transform from pillars to rods or ring structures.

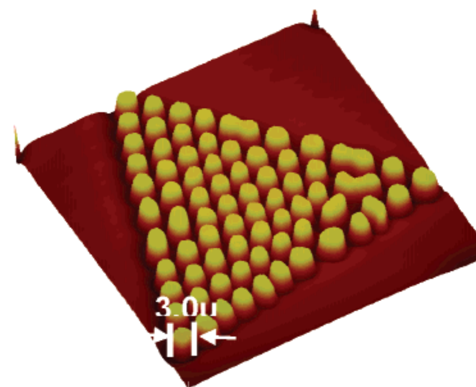

Figure 5. AFM image of PMMA–MAA pillar arrays transformed from a rod or cylinder array by heating to 200 °C.

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