Fabrication of Micro- and Nanoscale Polymer Structures by Soft Lithography and Spin Dewetting

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In this work, the process of spin dewetting of a polymer solution on a topographically patterned PDMS mold was used for fabrication of micro- and nanoscale polymer structures. Spin coating was used to provide a fast and reproducible coating. This simple technique was capable of producing a wide range of polymer feature geometries from a single microfabricated mold. This experimental study looks at the effects of the original mold feature geometry as well as the polymer solution concentration on the resultant microstructures. Polystyrene and poly(propyl methacrylate) were used as model polymers. Features with film thickness ranging from <100 nm to >5 \( \mu \)m were obtained using this technique. The process was also extended to fabrication of nanoscale features.

Introduction

Polymer microfabrication has become an integral part of microdevice development. The ability to fabricate polymer components from inexpensive, physically, and chemically versatile materials has led to a number of improved or new functionalities and broadened the applications of micro-devices. This has been especially true in the biomedical field where polymer materials provide improved biological interfaces as compared to standard microdevice materials. To this end, it is critical to have a wide range of simple and cost-effective polymer microfabrication techniques to provide flexibility and versatility in the fabrication of polymer microdevices.

Several microfabrication techniques have been developed for fabrication of polymer microstructures. Many of these are based on soft lithography.[1] Processes such as micromolding in capillaries[2] and microtransfer molding[3] have been developed for creating micro- and nanostructured polymer films or for producing independent polymer microstructures.

In addition to soft lithographic techniques, the process of polymer dewetting has also been used for polymer microfabrication. Dewetting is a phenomenon that has been well documented in thin polymer films.[4,5] In most cases, this is an undesirable effect that results in formation of holes in polymer films. However, researchers have begun to exploit this process to engineer surfaces that elicit a desired dewetting behavior for creating regularly structured polymer features. Primarily, this has been achieved by locally altering the chemical composition of the surface of interest.[6–9]

Dewetting of thin polymer films on chemically heterogeneous surfaces has been studied both theoretically and...
experimentally. The theory of polymer dewetting on chemically nonuniform surfaces has been described by Lenz and Lipowsky\cite{lenz10} and Komur et al.\cite{komur11} Microscale differences in the wettability of the substrate lead to instabilities in the film, which in turn leads to pattern formation. Experimentally, microcontact printing has been commonly used for inducing specific dewetting behavior. By printing hydrophilic chemistries on hydrophobic substrates, a hydrophobic polymer such as polystyrene (PS) will preferentially coat the hydrophobic regions of the substrate, thus creating a pattern.\cite{das06,moser06} A similar concept applies to printing of hydrophobic chemistries on hydrophilic substrates.\cite{das06,moser06}

In addition to chemically induced dewetting, surface topography is also known to be a factor in the dewetting process. The effects of physical, chemical, and physicochemical heterogeneities have been studied theoretically by Kargupta et al.\cite{kargupta12} Their model for physical dewetting was based on a sinusoidally rough surface and predicted polymer dewetting in the depressions of the rough surface. In contrast to chemically induced dewetting, physically induced dewetting is dominated by hydrodynamic interactions between the polymer solution and the topographically modified surface. Bao et al.\cite{bao13} used a combination of chemical patterning and topography for fabricating micro- and nanoscale poly(methyl methacrylate) (PMMA) and polycarbonate (PC) features. They coated a topographically patterned SiO$_2$ surface with a higher-surface energy silane on the raised surfaces and a lower-surface energy silane on the recessed surfaces. During spin coating, PMMA and PC coated the higher-surface energy areas. The polymer features were then removed from the raised features using heat and pressure.

Here we introduce the process of spin dewetting on topographically patterned poly(dimethylsiloxane) (PDMS) molds. This combination of soft lithography and physically controlled dewetting allows fabrication of polymer micro-features in both thin (<100 nm) and thick (>5 μm) polymer films without the need for chemical surface modifications. By spin coating, a topographically patterned mold with a polymer solution with the appropriate solvent and polymer content, micro- and nanoscale polymer features can be fabricated in a single-spin coating process. The spin coating process allows reasonably well-controlled coating conditions for patterning of microscale feature over a relatively large pattern area (>5 cm$^2$). While patterning of nanoscale features is less reliable over a large area, the same process shows promise for nanoscale fabrication as well. The lower reliability of replicating nanoscale features is likely due to inconsistencies in the original electron beam (e-beam) fabricated master and due to a relatively small original pattern area.

The spin dewetting process allows fabrication of features with either the same or different geometrical properties as the original mold depending on the polymer concentration used. Several levels of dewetting can be observed by altering polymer solution concentration. Complete dewetting takes place at relatively low polymer concentrations, and refers to the complete lack of polymer solution on the raised features of the PDMS molds. For complete dewetting, the polymer remains only in the recessed feature after the spin coating process. Partial dewetting occurs at higher polymer concentrations. In partial dewetting, the polymer separates during the spin process, resulting in filling of the recessed portions of the mold in addition to a second, physically separated polymer pattern that remains on the raised features of the mold. At even higher polymer concentrations, a continuous polymer film is formed on the PDMS mold.

Spin dewetting allows precise fabrication of polymer structures at the micro- and nanoscale with a single spin process. The dewetting process is initiated purely by surface topography, thus no chemical surface modifications are needed. This process could be applied to a number of applications as a simple method for fabricated physically independent polymer structures at the micro- and nanoscale.

**Experimental Part**

Poly(propyl methacrylate) (PPMA, MW = 150 000) (Scientific Polymer Products) and PS (melt flow index 4.0) (Aldrich) were used as model polymers. Polymers were dissolved in anisole (Sigma) at concentrations ranging from 0.125 to 20 wt.-%. From here on, all solution concentrations are given as wt.-%.

PDMS molds were fabricated using standard soft lithography procedures described previously.\cite{srinivasan14} Briefly, a silicon wafer was patterned with either S1813 or SPR220-7 photoresist (Shipley). S1813 and SPR220-7 were spin coated to achieve 1.4 and 7.5 μm thick films, respectively. Photoresists were patterned using UV photolithography with 2 μm circles in S1813 and 20 μm circles in SPR220-7. Nanoscale structures were fabricated using e-beam lithography. Silastic T-2 PDMS (Dow Corning) was mixed at a 10:1 ratio with T-2 curing agent and poured over the patterned wafers. The molds were cured at room temperature for 48 h before removal from the wafer.

The spin dewetting process is illustrated schematically in Figure 1. The PDMS mold was spin coated with a polymer solution at 3 000 or 4 000 rpm for 60 s. Spin speed and time were held constant for a given mold geometry to determine the effect of the pattern geometry and solution concentration on the resultant structures. Depending on the concentration of the polymer solution, periodicity of the pattern, and depth of the pattern, four potential coating scenarios are possible. Complete dewetting with intermediate separation between features is shown on the far left of Figure 1(a). In this case, the polymer solution dewets into portions of the recessed PDMS structure while some recessed areas of the PDMS mold remain uncoated. Complete dewetting with no intermediate separation occurs when the polymer solution coats...
the entire recessed portion of the mold but does not coat any of the raised portions of the mold. For partial dewetting, the entire recessed portion of the mold is coated and parts of the raised portion are also coated. In this case, there is a physical separation between the polymer within the recesses of the mold and the polymer coating the raised portions of the mold. Finally, the case of no dewetting occurs for higher polymer concentrations when the film completely coats the recessed and raised portions of the mold. Each of these scenarios is illustrated in a separate column in Figure 1(a).

To remove the polymer structures from the mold, the mold is inverted and heat and pressure are applied to remove the polymer from the mold onto the desired substrate. This is illustrated in Figure 1(b). For this study, polymer micro- and nanostructures were transfer onto glass or silicon substrates. The substrates were heated to 95 °C for PPMA and 170 °C for PS. Low pressure (≈2.5 psi) was used to remove features from the raised portion of the mold, and higher pressure (≈35 and 50 psi) were used to remove the features from the recesses of the 1.4 and 7.5 μm deep molds, respectively.

As shown in Figure 1(c), the resulting structures can have significantly different geometrical properties from the original mold. This allows features of multiple geometries to be fabricated from a single PDMS mold by varying polymer concentrations.

Resulting micro- and nanostructures were characterized using scanning electron microscopy (SEM) (Hitachi S-3000H), atomic force microscopy (AFM) (Veeco Dimension 3100), and optical microscopy.

Results and Discussion

Three-dimensional AFM images of PS microstructures fabricated using spin dewetting on 2 μm wide pillars are shown in Figure 2. The spacing between features is also 2 μm. Polymers solutions were spin coated at 3 000 rpm for 60 s. The images show the evolution of the feature geometry as the polymer solution concentration is increased. Figure 2(a) shows complete dewetting of a 0.125 wt-% polymer solution around the pillars with intermediate separation between the features. The resulting pattern consists of an array of physically separated polymer rings with 2 μm holes. At a solution concentration of 1%, the same basic structure is again observed, but the rings are interconnected with each of the adjacent rings. As the solution concentration is increased further, the wetting between the features increases until a continuous film is produced at a solution concentration of 3% [Figure 2(c)]. The pattern is a mesh with 2 μm through holes. The holes were verified by SEM (data not shown). Between solution concentrations of 3 and 4%, there was a transition from complete dewetting to no dewetting, and the polymer coated the entire surface of the PDMS mold. A solid film with 2 μm wells made from a 10% solution is shown in Figure 2(d).

Dewetting behavior was also studied on a PDMS mold with deeper features. In this case, the 7.5 μm tall features fabricated from SPR220-7 were employed. Solutions of PPMA ranging from 1 to 20 wt-% were spin coated at 3 000 rpm for 60 s. The coated molds were then characterized using optical microscopy. Evolution of the film morphology varied slightly from the 2 μm pillars due to the differences in both the thickness and lateral dimensions of the features. Figure 3(a) shows an uncoated PDMS mold. Figure 3(b–f) shows optical micrographs of spin coated PDMS molds at increasing polymer concentrations. The images show that for a low polymer concentration (1%), the polymer only coated the perimeter of the features.
20 μm pillar and at 3% the polymer coated the perimeter of the pillar and a portion of the area in between the pillars. This behavior is similar to that observed on the 2 μm pillars at low polymer concentrations. Partial dewetting was observed at concentrations of 5–15%. Figure 3 shows images of the coated mold at (d) 5% and (e) 15% polymer concentrations. The recessed features of the mold were coated with a continuous film while particles formed on the raised features of the mold. The particle diameter increased linearly from 2.4 to 3.6 μm with increased solution concentration (data not shown). This particle formation was not observed for 2 μm features. It is possible that the increased feature height and lateral dimension is needed to produce the necessary film instability to initiate the formation of particles on the raised features. At 20% concentration, the polymer formed a continuous film over the mold with no dewetting.

Figure 4 shows SEM micrographs of each step of the coating and removal process for a partially dewetted PPMA film on 20 μm PDMS features. Figure 4(a) is the original PDMS mold. Figure 4(b) shows the mold after spin coating. The image shows that the recessed area of the mold is almost completely filled with polymer and a physically separate polymer particle forms on top of the pillar. The image shows that the recessed area of the mold is almost completely filled with polymer and a physically separate polymer particle forms on top of the pillar. Figure 4(c and d) show the polymer particles that were removed from the top of the pillars using heat and low pressure and the mesh in between the features removed using heat and higher pressure.

The dewetting process was also demonstrated with nanoscale features. A pattern was first created using
e-beam lithography and the pattern was transferred to PDMS. The PDMS mold was then spin coated at 4 000 rpm with a 1% PS solution. Experiments indicate that in addition to the depth of the pattern, the lateral dimensions and the spacing of the pattern are also important parameters governing dewetting behavior. Figure 5 shows SEM micrographs of PS features after removal from the mold. For features with smaller lateral dimensions and a smaller center-to-center distance between features, complete dewetting was observed. For larger features with larger spacing, only partial dewetting was observed. The features in Figure 5(a) and 5(b) are approximately 170 nm separated by 300 nm and 250 nm separated by 500 nm, respectively. Note that no residual polymer is observed in (a) and small PS strips approximately 50 nm wide are located between the features in (b) for the same polymer concentration.

These results indicate that the original PDMS mold geometry (height, lateral feature dimensions, and spacing) and polymer solution concentration are all important factors in the formation of polymer features by spin dewetting. These features can have significantly different geometries from the original mold. This allows several different types of polymer features to be fabricated from a single PDMS mold. By properly engineering the mold surface, complicated polymer structures can be formed and tailored to a given application.

**Conclusion**

The process of spin dewetting has potential as a versatile and simple method of fabricating polymer micro- and nanostructures. Three different mold geometries were studied here. They can be categorized as thin film, thick film, and
nanoscale features. PS and PPMA were used as model polymers, but the process could potentially be applied to various soluble thermoplastic materials with minor process modifications. In this study, the effect of polymer solution concentration and mold feature geometry on final polymer microstructure was examined. It was found that dewetting occurs on all the three different patterns at differing polymer concentrations. For a given mold geometry, the dewetting transitions can be controlled by varying the concentration of the polymer solution. This results in polymer structures that can have geometries that are significantly different from the original mold. The process was applied to fabrication of microscale polymeric patterns and shows potential for application in polymer nanofabrication.

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Figure 5. SEM micrographs of nanoscale features. (a) No intermediate dewetting between features, (b) intermediate dewetting between features. P represents the primary features from the mold recesses and I the intermediate dewetted features.