

## Self-organized patterning of molecularly thin liquid polymer films utilizing molecular flow induced by ultraviolet irradiation

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A self-organized patterning method for molecularly thin liquid polymer films on solid surfaces has been demonstrated. In contrast to conventional methods that prepattern solid surfaces and then use the patterns as templates for polymer films, this method utilizes self-organization of polymers induced by ultraviolet (UV) radiation through a mask, thereby directly patterning the polymer films and omitting the pre patterning process. Such UV irradiation locally modified the interaction between polymer films and solid surfaces. As a result, molecular flow occurred at the boundary between the irradiated and nonirradiated areas, leading to three-dimensional surface structures.

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Patterning of liquid films using nonlithographic techniques has attracted interest due to lower costs and better suitability to devices made of polymer or overcoated with polymer films.<sup>1</sup> Liquid patterning is essential for the fabrication of electronic devices, optical storage media, and mechanical devices including microscopic fluidic devices such as micrototal-analysis systems or laboratory on chips.<sup>2</sup> Additionally, liquid patterning is important for improving the practical performance of micro-nanomechanical devices such as microelectromechanical systems (MEMSs) and computer hard disk drives (HDDs) because it allows local control of physical surface properties such as wettability, adhesion, and friction.<sup>3</sup> With the ever-increasing demand to shrink the lateral size of patterns, patterning of molecularly thin liquid films is becoming a significant concern due to the difficulty of fabricating patterns with high aspect ratio. Different from thick liquid films, the behaviors of nanometer-thick liquid films such as thickness distribution are strongly dependent on interfacial interaction with solid surfaces.<sup>4</sup> It is thus possible to pattern molecularly thin liquid films by locally modifying the strength of the interfacial interaction. This can be accomplished using two methods. One modifies the solid surfaces first and then uses them as templates for the liquid films; the other directly modifies the interaction between solid surfaces and liquid films. The former has been intensively studied and the patterning capability at micrometer and nanometer scales has been demonstrated.<sup>5-8</sup> In such methods, however, the solid surfaces must be deliberately prepatterned to generate heterogeneous surface properties. This poses a limitation on the materials of the solid surfaces because achievable surface properties are determined by material properties. Additionally, pre patterning might be time consuming. In contrast, by utilizing the self-organization of polymers, the latter method directly patterns thin liquid films without the pre patterning process; however, it has not been studied and reported to date. In this study, we present a self-organized patterning method in which interfacial interaction

is directly modified by irradiating molecularly thin liquid polymer films coated on solid surfaces with ultraviolet (UV) radiation through a mask. Such irradiation is expected to generate a gradient in disjoining pressure (i.e., the negative gradient of surface energy with respect to film thickness)<sup>9</sup> at the boundary between the nonirradiated and irradiated areas. Driven by the disjoining pressure gradient, film thickness will redistribute, thereby leading to three-dimensional surface structures.

Amorphous-hydrogenated carbon (*a*-CH) overcoats of 3-in.-diam magnetic disks were used as solid surfaces. The *a*-CH overcoat was deposited using a plasma-enhanced chemical vapor deposition method. It had a thickness of 4.5 nm and an average surface roughness of 0.36 nm. Perfluoropolyether (PFPE) lubricant (Fomblin AM3001, Solvay Solexis) was used as the sample liquid. The lubricant is a linear chain polymer, featuring the UV light-absorbing piperonyl group at each end of the chain.<sup>10</sup> The molecular weight and polymer length are about 4000 g/mol and 14 nm, respectively. The PFPE polymer films were dip coated onto the solid surfaces by briefly immersing the solid surfaces in a PFPE solution diluted with a hydrofluoroether solvent (HFE-7200, 3 M) and then withdrawing it from the solution. Applied film thickness could be controlled by the concentration of the PFPE solution and by the speed of withdrawal from the solution.

Subsequent to film deposition, the solid surface was treated inside a nitrogen-purged chamber by UV irradiation through a mask, as illustrated in Fig. 1. The mask was comprised of a 2.3-mm-thick glass substrate with 73-nm-thick Cr and 32-nm-thick CrO layers. As depicted in Fig. 1 a 50×50 mm<sup>2</sup> transparent window and two 50×50 mm<sup>2</sup> stripe patterns were formed on the mask. The stripe patterns had transparent and opaque regions, with linewidths of 100 and 20 μm, respectively, arranged at equal intervals. A dielectric barrier discharge excimer lamp (USER20-172B, Ushio) that provided UV radiation at 172 nm was used as the light source. The distance between the lamp and the disk was set to 5 mm and UV irradiation time to 20 s. Because there

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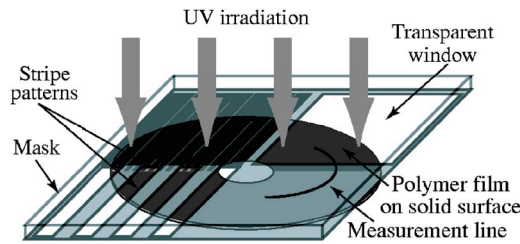


FIG. 1. UV irradiation through a mask and measurement of UV-induced change in distribution of polymer films. Using the transparent window on the mask, only half of the polymer film is irradiated, and thickness profiles of the film are measured at positions indicated by the arc line at different times.

was no collimating optical system in the UV irradiation apparatus, the mask was placed in close proximity to the disk to avoid pattern blurring caused by oblique incident light beams.

It is supposed that the thickness distribution of the PFPE films may have changed after UV irradiation because of modifications to the interactions between PFPE and the solid surface. Thus we measured the time-dependent thickness profiles in the nonirradiated and irradiated regions using a scanning ellipsometer (MARY-102, Five Lab) that had a thickness resolution of 0.1 nm and a spatial resolution of 30  $\mu\text{m}$ . As shown schematically in Fig. 1, utilizing the 50  $\times$  50 mm<sup>2</sup> transparent window and the opaque area on the mask, only half of the PFPE film was irradiated, and its thickness profiles were measured at positions indicated by the arc line ( $R=20$  mm,  $\theta=30^\circ-150^\circ$ , and  $\text{step}=0.1^\circ$ ) at different times. Figure 2 only shows the results measured at 0, 5.5, and 47.5 h after UV irradiation for simplicity. The initial profile measured just before UV irradiation is plotted with a black solid line for comparison. Additionally, the black dotted line represents the distribution of bonded thickness measured using the ellipsometer after rinsing the lubricated solid surfaces in solvent HFE-7200 with ultrasonic cleaning. It is seen from Fig. 2 that, as time proceeded, the film in the nonirradiated region spread toward the bare disk surface and the film thickness decreased. We speculate that the decrease in film thickness originates from the polymer relaxation process in which the conformation of the polymers transits to a

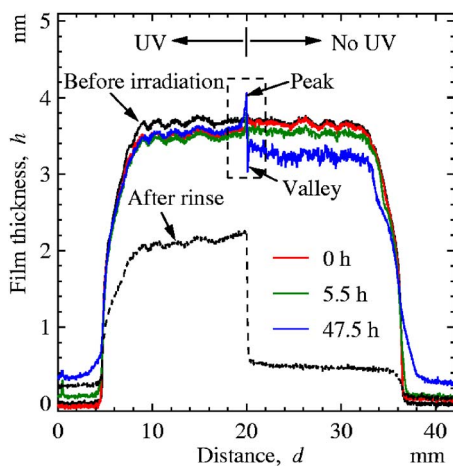


FIG. 2. (Color online) Time-dependent film thickness profiles in UV-irradiated and non-UV-irradiated regions. The black solid and dotted lines are profiles measured just before irradiation and after rinsing the film in solvent with ultrasonic cleaning, respectively.

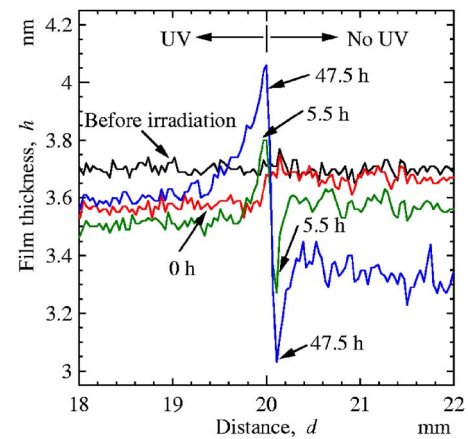


FIG. 3. (Color online) Expansion of region enclosed by a dashed box in Fig. 2.

more stable compressed form due to polymer/surface interactions.<sup>11</sup> In the irradiated region, film spreading decelerated significantly, and film thickness changed only slightly with time, although it did decrease upon irradiation. In addition, average bonded thickness in the irradiated area was more than 2 nm, far thicker than the thickness of 0.5 nm in the nonirradiated area. These characteristics are basically the same as previously reported,<sup>11</sup> demonstrating UV irradiation strengthens the interactions between polymer films and solid surfaces. The most interesting phenomenon observed in Fig. 2 is the development of a peak and valley at the boundary between the irradiated and nonirradiated regions. To allow for detailed examination of the peak and valley features, the region enclosed by a dashed box in Fig. 2 is expanded in Fig. 3. Before UV irradiation, the polymer film was uniformly distributed. After irradiation through the mask, however, polymers in the nonirradiated area flowed toward the irradiated area, resulting in the 1-nm-high peak/valley structure. Note that this phenomenon of UV-induced molecular flow was also confirmed for 2-nm-thick films.

In the microscopic regime governed by surface forces, the disjoining pressure gradient is the major driving force for spreading of a liquid film.<sup>12</sup> Disjoining pressure is defined as the negative gradient of surface energy with respect to film thickness as follows:<sup>9</sup>

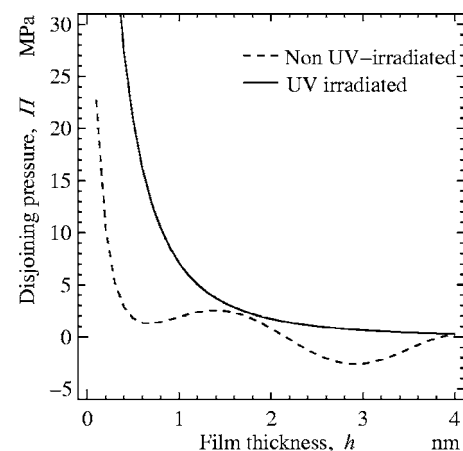


FIG. 4. Comparison between disjoining pressures of nonirradiated (broken line) and irradiated (solid line) polymer films.

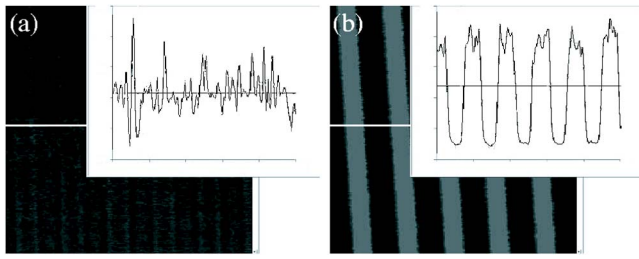


FIG. 5. Patterning of a 3.7-nm-thick polymer film with stripe of 100  $\mu\text{m}$  in linewidth (insets are cross-sectional profiles along the central lines). (a) Immediately after UV irradiation. (b) 47.5 h after UV irradiation.

$$\Pi = \Pi_d + \Pi_p = -\frac{d\gamma_s^d}{dh} - \frac{d\gamma_s^p}{dh}. \quad (1)$$

To investigate the UV-induced change in disjoining pressure, we measured surface energies with respect to applied film thickness for nonirradiated and irradiated films. The surface energies were calculated from sessile drop contact angles measured by a contact angle meter (Model CA-X, Kyowa Interface Science). Using the Owens and Wendt equation, the dispersive and polar surface energy components, respectively, of the lubricated solid surface were determined from the contact angles made with the surface by hexadecane and water, and the total surface energy was then obtained from the sum of the two components.<sup>13,14</sup> Figure 4 compares disjoining pressures  $\Pi$  of the films with/without UV irradiation, obtained by differentiating the fitted curves of the measured total surface energies. In the entire investigated thickness range of 0–4 nm, the disjoining pressure of irradiated films is higher than nonirradiated films. This result rationally explains the UV-induced molecular flow from nonirradiated toward irradiated areas, because it is commonly known that a liquid film spreads from a region of low disjoining pressure toward a region of high disjoining pressure.<sup>12</sup>

Employing the molecular flow between UV-irradiated and nonirradiated regions, liquid polymer films can be patterned to three-dimensional structures. For confirmation, we irradiated 3.7-nm-thick PFPE films coated on *a*-CH surfaces with UV through stripe patterns of 100 and 20  $\mu\text{m}$  in linewidth. UV-induced changes in thickness distribution of the films were monitored using an optical surface analyzer (OSA5130, Candela Instruments) that had a high spatial resolution of 5  $\mu\text{m}$ . Figure 5 exemplifies a stripe pattern of 100  $\mu\text{m}$  in linewidth. The bright and dark areas in the figure represent thin and thick film areas, respectively. Immediately after UV irradiation, as shown in Fig. 5(a), redistribution of film thickness was only observed in the vicinity of the irradiation boundary, and therefore the pattern remained unclear. At 47.5 h after UV irradiation, as presented in Fig. 5(b), a distinct stripe pattern was obtained. Currently, the minimum lateral size of the patterns is restricted by oblique incident light beams and light diffraction. This can be overcome by improving the performance of the UV irradiation apparatus and hence patterns of several micrometers or submicrometers are expected to be realized. However, when the size of patterns shrinks to nanometer scale which is comparable with the size of liquid polymers, the self-organization of the polymers may become unstable, possibly imposing a limit to the achievable minimum lateral pattern size. It should be noted

that, however, due to the limited spatial resolution (5  $\mu\text{m}$ ) of the OSA, we could not observe the pattern in detail at the present stage. It is also difficult to directly observe the liquid patterns using conventional highly resolving methods such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). Solid replicas must be prepared to allow for the SEM or AFM observation. Besides the complicatedness, a significant concern is that the replication process may not preserve the surface structures of the patterned liquid films since the nonbonded mobile polymers are not stable and may be easily damaged.<sup>15</sup> Therefore, further investigation is necessary to evaluate the fineness and the achievable minimum lateral size of the patterns formed using our method.

The molecularly thin polymer films patterned with our method possessed a unique three-dimensional structure. Nonbonded mobile polymers moving from nonirradiated regions accumulated on polymers firmly bonded to the solid surface in irradiated regions, with residual mobile polymers stored in the nonirradiated regions. Such structures are supposedly capable of diminishing adhesion and providing better cushioning and protection performance against contact sliding. It is thus possible to use such patterned polymer films as lubricants for devices that require reliable nanoscale relative motion, as in MEMSs and HDDs. Especially in HDDs, the spacing between the magnetic disk and the read/write head must be minimized to maximize recording density, and contact recording at zero spacing is most desirable. The patterned polymer films presented in this work may provide solutions to the lubrication problems that are the bottleneck for realizing contacting recording systems.

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