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Unusual surface reliefs from photoinduced creeping and aggregation behavior of azopolymer

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We report the spontaneous formation of unusual surface reliefs, in which two sets of sinusoidal gratings were hierarchically structured, merely by single-step holographic inscription on amorphous azopolymer films. By monitoring of growth behavior of surface reliefs during holographic inscription, we found that the formation of additional grating is caused by the creeping and resulting aggregation of dome structures. Our direct observation of creeping and aggregation behavior is expected to contribute to enhancing the understanding of unusual surface reliefs, and also in fabricating complex surface reliefs. © *2008 American Institute of Physics*.
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Various photophysical and photomechanical phenomena, based on the photoisomerization of azobenzenes, have been reported in recent years, including light-controlled self-assembly,[1] reversible changes in fluid viscosity,[2] tuning of the photonic bandgap,[3] and photoswitched wettability.[4] When the azobenzene molecules are incorporated into polymer chains, their reversible photoisomerization gives rise to the macroscopic polymeric motions, which in turn results in photoinduced bulk mass transfer,[5–7] reversible volume change,[8] and bending behavior.[9] Especially, photoinduced bulk mass transfer has attracted considerable attention because this phenomenon provides us with an effective approach for the fabrication of surface reliefs. Such surface reliefs have many significant applications in micro/nanopatterning.[10–12] Recently, we reported the facile method of fabricating close-packed microlens arrays using photoinduced surface reliefs as templates.[13]

The surface reliefs can be easily fabricated by single-step holographic inscription with azobenzene polymer (azopolymer) film.[5–7] When intensity or polarization interference patterns are imaged onto azopolymer film, either amorphous or liquid crystalline, sinusoidal grating patterns or two-dimensional periodic patterns are produced spontaneously at temperatures well below T_g. Generally, depending on the polarization and light intensity, the depth of surface reliefs can reach several hundred nanometers, and the period of surface reliefs can be well defined in the range of hundreds of nanometers to several micrometers by precise controlling incident angles of writing beams.[7] The surface reliefs can be recovered to original state by heating the azopolymer film above T_g or irradiating a single beam with proper wavelength and polarization.[14] Over the years, the fundamental aspects related to the formation of surface reliefs on azopolymer film are basic interest, and various mechanisms have been proposed to explain these phenomena.[15–18] However, the underlying formation mechanisms are not still understood completely.

Recently, several research groups reported interesting and unusual type of surface reliefs such as hexagons and superhelixlike patterns,[19,20] and the analyses of these phenomena indicated that photoinduced organization of azobenzene molecules plays an important role in the formation of unusual surface reliefs. In this letter, we demonstrate unusual hierarchical surface reliefs, where two sets of sinusoidal gratings with different grating vector and period were hierarchically structured on amorphous azopolymer films. These hierarchical structures were spontaneously produced merely by the single-step irradiation of interference patterns under specific experimental conditions. Main grating was developed from the interference pattern as expected, whereas the formation of additional grating was based on the other mechanism that involves creeping and aggregation of dome structures. This current work is expected to contribute to making an important advance in understanding of the unusual typed surface reliefs as well as the fabrication of well-registered complex surface reliefs.

By way of demonstration, we performed holographic inscription at the three polarization modes: (*s*-:*s*-), (±45°), and orthogonal circular (OC) (Fig. 1). The (*s*-:*s*-) mode is light intensity interference pattern, whereas both (±45°) mode and (OC) mode are polarization interference patterns. The incident angle and total exposure energy of the irradiation were 7° and 7.8 J/cm^2 (beam intensity was 2.6 mW/cm^2), respectively. Detail optical setup for the holographic inscription is described in previous work.[13] The epoxy-based azopolymer, abbreviated as PDO 3, was used as amorphous azopolymer.[7,13] The azopolymer films were prepared by spin coating, and their thickness was controlled to 300 nm. Figure 2 shows the atomic force microscopy (AFM)

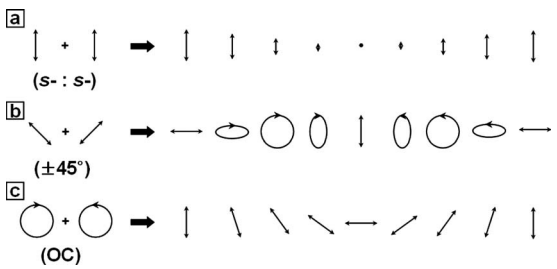

FIG. 1. Schematic illustration of polarization modulation of interference pattern: (a) (*s*-:*s*-) mode, (b) (±45°) mode, and (c) orthogonal circular (OC) mode.

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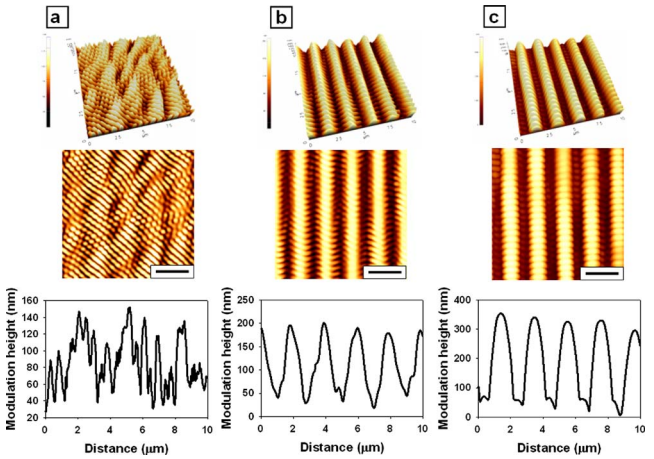

FIG. 2. (Color online) Surface reliefs and their cross-section profiles in the horizontal direction of AFM images: (a) (s-:s-) mode, (b) ($\pm 45°$) mode, and (c) OC mode. In each case, three-dimensional (3D) AFM images (top), two-dimensional (2D) AFM images (middle), and cross-section profiles (bottom) are described. The scale bars represent 2.5 μm.

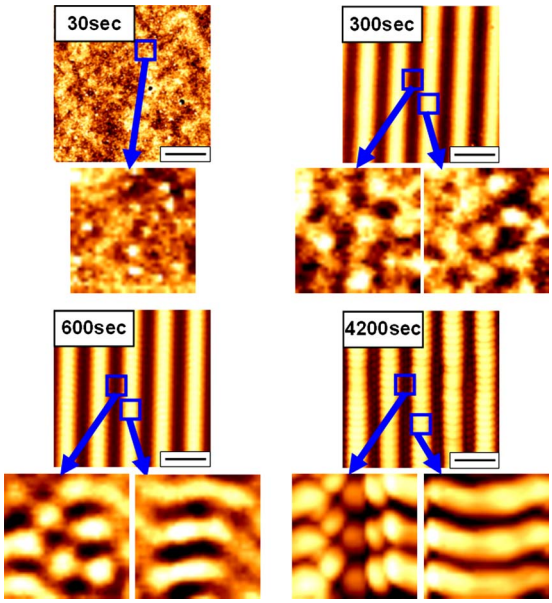

FIG. 3. (Color online) AFM images of surface reliefs developed by the irradiation of interference patterns with OC mode as function of exposure time. The scale bars represent 2.5 μm.

(PSIA XEI-100 systems) images of obtained surface reliefs from PDO 3 films and their modulation heights of main gratings. For (s-:s-) mode, the domes or partially elongated domes were observed in addition to weakly formed main grating, and the elongation occurred in the 45° tilted direction with respect to s-pole [Fig. 2(a)]. These results resemble most closely hexagons of C. Hubert *et al.* obtained by single-beam irradiation.[19] In contrast, it is very striking that the irradiations of polarization interference patterns with such modes of ($\pm 45°$) mode and (OC) lead to the unusual surface reliefs in which two sets of sinusoidal gratings were hierarchically structured [Figs. 2(b) and 2(c)]. In particular, the main grating showed same period (2 μm) and grating vector as those of the interference patterns as expected, but additional grating did have different period and grating vector from those of the interference patterns (herein, theoretical period of interference pattern was calculated by Bragg's law).[20] Earlier analyses of unusual surface reliefs such as hexagons and superhelixlike patterns indicate that light-induced orientation of azobenzene molecules according to the polarization of incident beams and resulting aggregation could play an important role in the process, as is evident from the dependence of structure orientation on the polarization of incident beam.[19,20] However, this approach is not applicable to our observations because the additional grating vectors, for both ($\pm 45°$) mode and (OC) mode, do not depend on the spatially distributed polarization vector, but oriented only in the direction perpendicular to that of main grating vector [Figs. 2(b) and 2(c)]. Therefore, it is reasonable to expect that another key factor is involved in this process.

To verify the factor playing an important role in our phenomenological finding, it should be noted that the polarization of interference pattern significantly influence on the degree of bulk mass transfer of azopolymer across interference pattern as well as the orientation of azobenzene molecules. According to the previous report, ($\pm 45°$) mode and (OC) mode lead to larger bulk mass transfer of azopolymer than (s-:s-) mode.[7] As a result, modulation heights of gratings derived from ($\pm 45°$) mode and (OC) mode are higher than that derived from (s-:s-) mode. Indeed, for (s-:s-) mode, smaller modulation height of 40 nm was obtained, whereas ($\pm 45°$) mode and (OC) mode gave rise to higher modulation heights (150–300 nm), as shown in Fig. 2. By comparing morphologies and modulation heights described in Fig. 2, we find that the degree of bulk mass transfer strongly affects whether the formation of additional grating will occur. In the case of the (s-:s-) mode, the obtained morphology closely resembled the hexagons that are caused by single-beam irradiation as already mentioned.[19] This is due to the fact that (s-:s-) mode induces negligible bulk mass transfer, similar to the single beam irradiation. On the other hand, for ($\pm 45°$) mode and (OC) mode, additional gratings were clearly observed under relatively larger bulk mass transfer, compared to (s-:s-) mode. Therefore, it is obvious that bulk mass transfer plays a key role in the formation of additional grating.

In order to elucidate bulk mass transfer contribution on the formation of additional gratings in greater detail, we monitored the growing behavior of hierarchical surface reliefs during holographic inscription. We employed (OC) mode as the polarization of writing beam with intensity of 2.6 mW/cm^2. Figure 3 displays the exposure time evolution of hierarchical surface reliefs in azopolymer films. At the initial state of holographic inscription (300 s), only individual domes were generated on the weakly formed main grating (sinusoidal grating). However, it is clearly seen that individual domes on the peaks of main grating crept, and consequently aggregated as exposure time increases, while domes on the troughs of main grating remained. More importantly, it is worth noting that creeping and aggregation occurred only in the direction of bulk mass transfer as is evident from the absence of creeping in the vertical direction. These results indicate that the formation of additional grating is originated from the bulk mass transfer-induced creeping and aggregation, during holographic inscription. This direct observation of creeping and aggregation behavior allows us to make substantial forward steps in the understanding of unusual surface reliefs. Furthermore, these bulk mass transfer-induced transformations of dome structures can be useful for the fabrication of well-registered complex

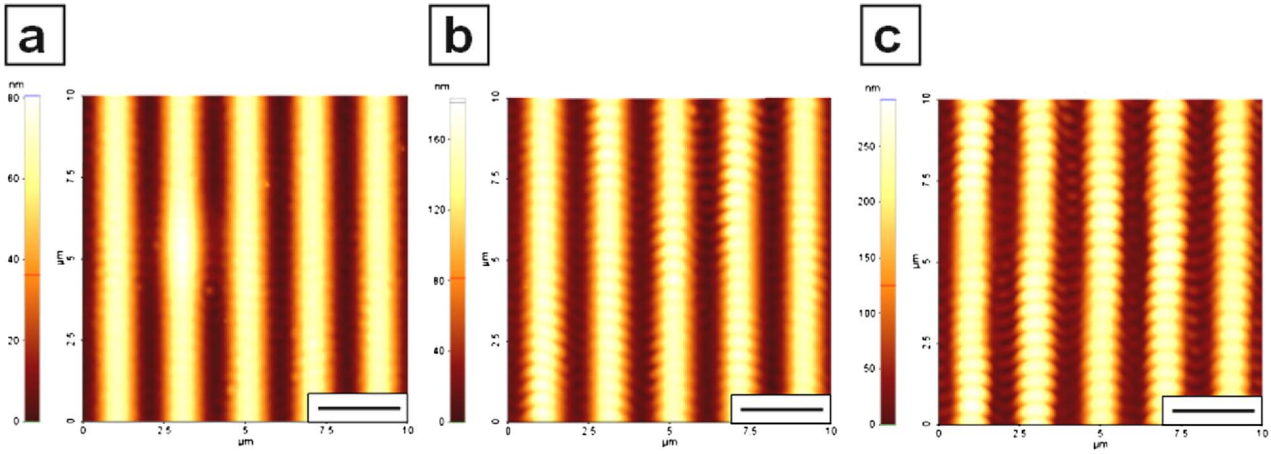

FIG. 4. (Color online) Surface reliefs as function of beam intensity: (a) 0.236 mW/cm^2 (b) 0.648 mW/cm^2, and (c) 1.200 mW/cm^2. The scale bars represent 2.5 μm.

structures such as quasicrystals and hierarchical structures. To generate such structures, we will focus on the control of creeping and aggregation behavior. The details will be reported in a forthcoming paper.

A final consideration is that the beam intensity used in our experiment (2.6 mW/cm^2) was relatively weak compared to that used in previous studies of azopolymer including the irradiation of single-beam and two-beam interference. Generally, beam intensities from several ten mW/cm^2 to several hundred mW/cm^2 have been used in this kind of study.[5–7,19,20] Especially, in the case of hexagons formed on the azopolymer films with 300 nm thickness that is coincident with the thickness used in our study, no structures (domes) were observed, if the beam intensity is lower than 200 mW/cm^2.[19] To further study the intensity dependency, we measured morphologies of azopolymer as function of beam intensity. The exposure time and polarization were 3800 s and (OC) mode, respectively. In our experiment, contrary to the early study, incident beam even with extremely weak intensity (0.236 mW/cm^2) also caused the formation of additional grating as shown in Fig. 4(a) (additional grating was weakly observed). Furthermore, the beam intensity at saturation point of additional grating growth [Fig. 4(c)] was also very small (1.2 mW/cm^2). This unusual intensity dependency compared to conventional study is unclear now, but possibly related to several differences of experimental conditions between previous and present work, for example, type of azopolymer materials [co(DR1/MMA) versus PDO 3] and irradiation condition (single-beam irradiation versus interference beam irradiation).

In summary, we have studied the formation of unusual surface reliefs marked by the presence of additional grating as well as main grating. From the monitoring of growth behavior, it can be concluded that bulk mass transfer of azopolymer during holographic inscription leads to the creeping and aggregation of domes formed on the azopolymer surface, and then additional grating is generated. We believe that our observations and analyses could provide a substantial contribution to understanding of photoinduced migration of azopolymers and fabricating a number of complex, but innovative, micro/nanostructures.

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