Controlling spontaneous surface structuring of azobenzene-containing polymers for large-scale nano-lithography of functional substrates

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In this work, we investigate the effect of illumination parameters which is light polarization, wavelength, and beam focalization, on the large-scale patterning of the surface of azobenzene-containing polymer films by means of spontaneous surface structuring. This is a phenomenon due to the interference at the sample surface between different light modes originated by scattering from the primary illuminating beam. In particular, the surface patterning in regions of a few squared millimeters with a spatial resolution down to 180 nm is achieved by means of a single beam illumination. The realized topographical structures are both preferentially oriented gratings and isotropically distributed topographical protrusions (dots), with sub-wavelength features. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4794398]

In the last fifteen years, lots of experiments have been carried out to investigate the intriguing phenomenon of mass-migration occurring on the free surface of azobenzene-containing polymer films when illuminated by either light interference patterns or by focused laser beams.[1–3] In particular, the sample surface morphology is altered with the appearance of protrusions and hollows as a consequence of material displacement along the light polarization direction, preserving indeed the polymer volume on the mesoscopic length scale. Several models have also been proposed[4–6] although no one gives a complete description of all the features reported for the mass-migration phenomenon. Recently, we reported the experimental observation of spiral-shaped relief patterns on the surface of an azo-polymer illuminated with a laser beam having a helical wavefront.[7] We found an explanation for our observation that links them to an unexpected, polymer mediated, interference effect between longitudinal and transverse field components at the polymer surface.

However, the light-induced morphology modulation in azo-polymer films has already been exploited for high-density data storage[8] as well as for optical nano-imaging.[9] Moreover, very recently, Kravchenko *et al.*[10] achieved one- and two-dimensional silicon nanostructuring by using photo-induced surface relief gratings as lithographic masks instead of conventional photoresist. As functional substrates in biological applications, Barillé *et al.*[11] used a patterned bio-compatible azo-polymer film as reconfigurable scaffold for cells network formation.

For these recent applications, large-scale patterning is a crucial feature.[12] In particular, a single beam process would be preferable with respect to multiple beams interference that is a more complex illumination scheme, affected by the mechanical stability of both optical components and sample. Single beam laser-induced surface structuring is indeed well known in research from years (for instance, see Ref. 13 and references therein) and has been applied on several materials. The technique consists in originating a light pattern at the sample surface by exploiting the interaction of the primary illuminating beam with secondary waves that can arise at the surface (plasmonic waves, guided modes, and leaky modes) or modes originated by local scattering by surface defects. The phenomenon is then an interference process in between different light modes originated at the sample surface from the illuminating primary wave. According to the photo-response characteristic of the sample (local heating due to light absorption, light-induced photo-reaction, etc.), the surface morphology is then modified with the appearance of irregularities. After the early state of the process, the periodicities of the irregularities are restricted to those suitable to additionally diffract the primary beam light, sustaining a *spontaneous* feedback mechanism that sets the final modulation of the sample surface.

Single beam surface structuring of azobenzene polymers has already been shown both using a continuous[14–18] as well as a pulsed laser source[19,20] and even by activating the process by exploiting two-photon absorption of a symmetric donor-acceptor-donor structured Y-shape azo-polymer.[21] In this Letter, we show how spontaneous surface structuring of azo-polymer films under single beam exposure can be controlled by tuning the illumination parameters. This allows changing the pattern morphology and periodicity until obtaining squared millimetres patterned areas containing nanometric-sized structures.

The polymer film used in our experiments is an acrylic polymer bearing the photoresponsive moieties as side chains of the polymeric backbone (for details about the synthesis, see Ref. 7). Thin films of polymer (typical thickness $<1\ \mu$m) were spin coated onto 170 μm thick microscope coverslips.

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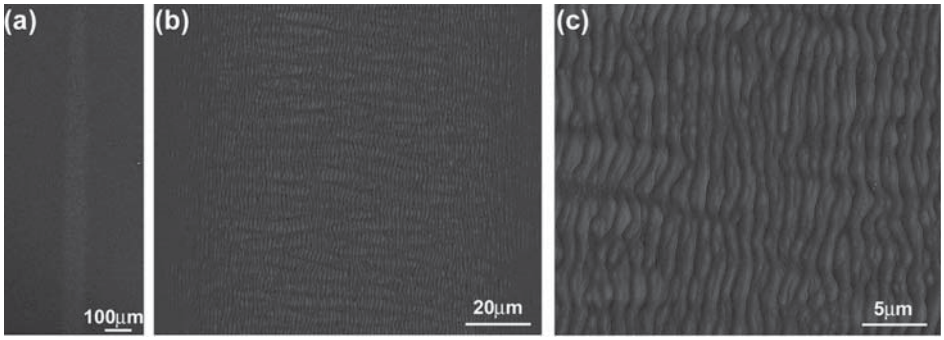

FIG. 1. (a)-(c) SEM micrographs of an elliptical-shaped patterned area, obtained by focusing the laser beam with a cylindrical lens.

The material absorption spectrum shows a broad maximum peaked around 350 nm, in the near-UV, as is expected for polymers containing azobenzene moieties. The sample morphology was investigated both by scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM analysis was performed by using a Nova NanoSEM 450 system (FEI), whereas for AFM, a XE-100 (Park Systems) was used.

In our experiment, we first used a linearly polarized Ag^+ laser beam of 488 nm emission wavelength. The laser beam was first expanded into a collimated beam of about 3 mm in diameter. The beam was then focused on the sample surface by means of a 75 mm focal length cylindrical lens. There was then a preferential focusing plane (the plane containing the short radius of the cylindrical lens) and the laser spot at the sample surface resulted into an elliptical spot a few millimeters long (width about 0.15 mm). Figure 1(a) shows a SEM image of part of the elliptically patterned area, obtained by exposing the sample to the focused laser beam for 90 min. The samples were coated by a thin layer of Cr ($<$10 nm) prior to SEM analysis. SEM images at higher magnifications (Figs. 1(b) and 1(c)) reveal the presence of a structured surface morphology in the illuminated region.

In the employed illumination conditions, the light polarization direction can be changed between two orthogonal polarization directions (by means of a half waveplate) parallel or perpendicular with respect to the focalization plane. Figures 2(a)–2(c) show the surface modulation (atomic force microscopy micrograph (a) and SEM (c)) obtained when the light polarization direction is parallel to the plane of focalization, whereas Figures 2(d)–2(f) display the results for a polarization direction perpendicular to the focalization plane. In both conditions, the topographical gratings are characterized by two periodicities. These results evidence that in our experimental conditions, spontaneous surface structuring is mainly driven by the polarization state of the incident light, whereas the beam focalization has a minor influence on the obtained pattern morphology. However, the light focalization allows increasing the light optical density (the power of the non-focused beam is of about 2 mW). The two main periodicities observed in the spontaneous structures are of about 444 nm and 1.3 μm. The spatial frequencies distributions around these two periodicities for incident polarization parallel and perpendicular to the laser stripe are evidenced by the two-dimensional Fourier transform diagrams, displayed in Figs. 2(b) and 2(e), respectively.

Figure 3(a) shows the surface modulation obtained by focusing the laser beam by means of a spherical lens of 125 mm focal length. The results are similar to those obtained with a cylindrical lens: The grating vector is along the polarization direction but the laser spot as well as the patterned area are circular (not shown in the figure). Figure 3(b) shows the result of modifying the polarization state of the incident laser into a circularly polarized state by means of a quarter waveplate. The morphology of the sample surface after exposure is more complicated. In particular, a grating similar to those examined above is formed along the direction of the fast axis of the quarter waveplate. The observed grating is likely due to residual linear polarization along the direction of the fast axis of the $\lambda/4$ waveplate. Indeed, a further structuring can be observed, constituted by mostly equally separated topographical features (dots). These

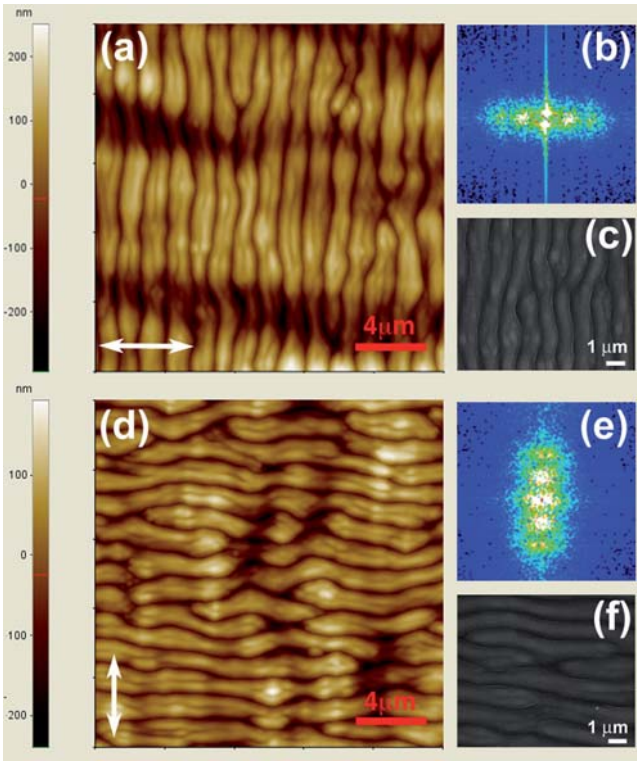

FIG. 2. (a) Oriented topographical grating resulting by illumination with light whose polarization direction is parallel to the white arrow in the picture and corresponding two-dimensional Fourier transform (b). (c) SEM picture of the sample shown in (a). (d) Topographical grating obtained when the light polarization is 90° rotated with respect to the condition of picture (a). The grating vector is always oriented along the light polarization direction. (e) Two-dimensional Fourier transform of the topographical maps shown in (d) and SEM picture of the sample (f).

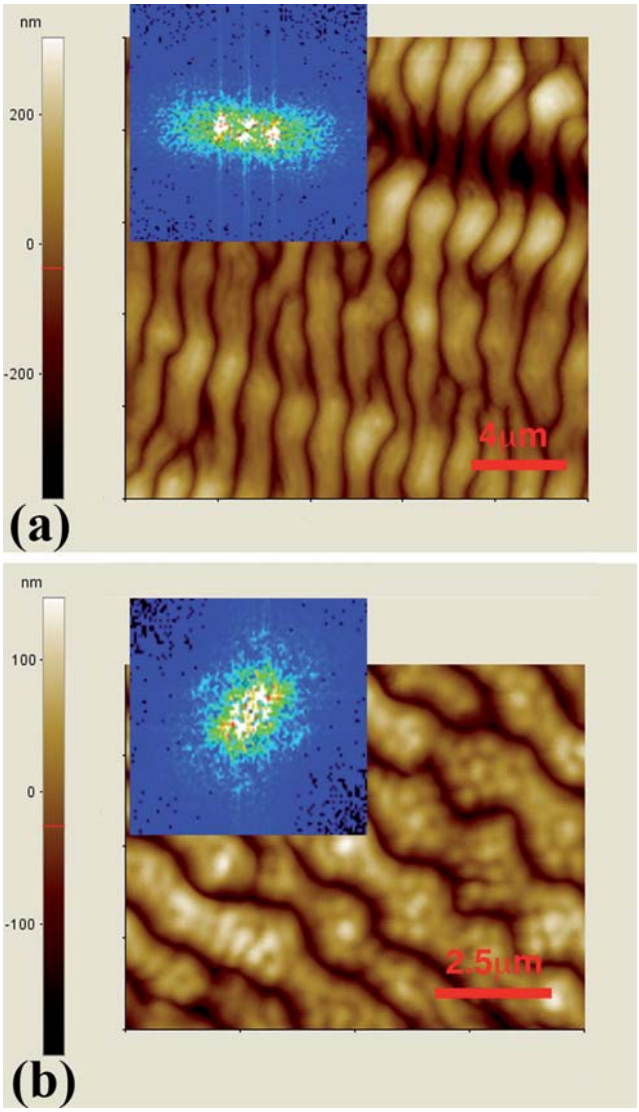

FIG. 3. (a) Topographical grating oriented along the light polarization direction when the linearly polarized beam is focused by means of a spherical lens. (b) The same as for (a) when the light beam is circularly polarized with residual linear polarization along the grating vector. The pictures' insets show the two-dimensional Fourier transform of the topographical maps shown in (a) and (b).

regular structures, homogeneously distributed in all directions, are a consequence of the circularly polarized component of the beam.[14] In fact, in the case of circularly polarized light, there is no preferential polarization direction and the diffraction at the surface is isotropic as well as the polymer mass-migration and the resulting structuring, since activated by the azo-moieties isomerization that is more likely to happen when chromophores are aligned along the polarization direction.[7,22] The spacing in between adjacent topographical dots is close to the light wavelength, similarly to the short periodicity described above, obtained with linearly polarized light. However, the full width at half maximum (FWHM) of a single dot resulting from this isotropic surface modulation is of only 360 nm.

Motivated by the observations with circularly polarized light at 488 nm, we changed the light source aiming at reducing the dimensions and spacing of the topographical structures and improving the patterning homogeneity. To this aim, we used a pulsed nitrogen laser ($\lambda = 337$ nm). This is a laser mounting a nitrogen cartridge as active medium. The laser has a nominal peak power of 170 μJ, pulse width of less than 3.5 ns, and a repetition rate of 20 Hz. The polarization degree of the laser is indeed very low and close to a non-polarized light source.[23] The light from the laser is focused on the sample surface by means of the 75 mm cylindrical lens, already used with Ag^+ laser (Figs. 1 and 2). Figure 4 shows the resulting sample surface structuring after exposure. The topographical features are dots uniformly distributed on the sample surface. This is evidenced by means of the two-dimensional Fourier transform (reported as picture's inset) that is perfectly symmetric in all directions. The main spacing distance in between the dots is again close to the laser wavelength whereas the FWHM is as small as 180 nm.

Controlling the illumination parameters (focusing and polarization) in our experiment results in the possibility to easily obtain large-scale patterning of azobenzene-containing polymer films that can be used as functional substrates for a number of applications. In particular, using a cylindrical or spherical lens affects the shape of the patterned area. The polarization state of the light beam allows designing oriented gratings, homogeneously distributed protrusions, or a combination of both of them. The laser wavelength instead determines the periodicity of the surface modulation and the resulting dimensions of the protrusions. Our results demonstrate that patterning on larger areas (of the order of cm^2) is feasible, possibly by successive exposure of adjacent regions. To this aim, one has to consider the intensity dependence of the feature height, which can be easily appreciated at the border of the exposed region shown in Fig. 1(b). Due the Gaussian shape of the focussed beams, increase of the features height from 10 nm to 120 nm is

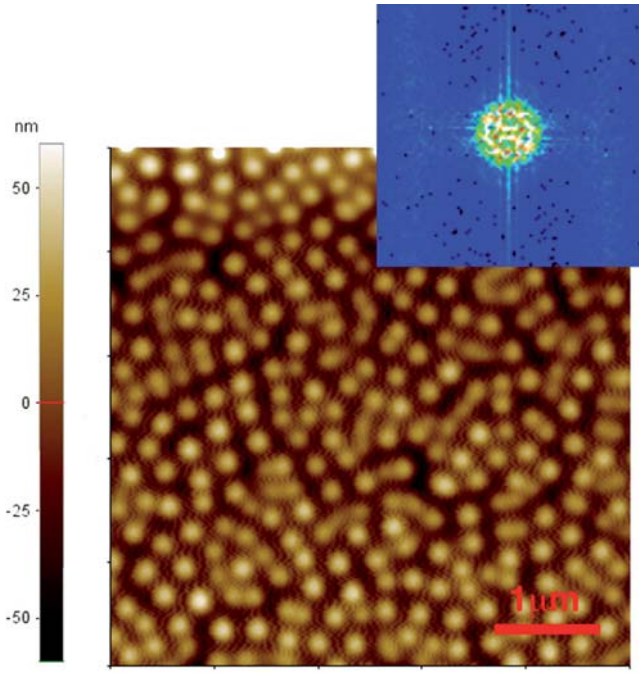

FIG. 4. Spontaneous surface structuring resulting from illumination by means of a 337 nm wavelength laser beam with a low polarization degree. The mean size of each topographical feature (dots) is of about 180 nm.

measured at the border of the exposed region, over a distance of about 15 μm (about 10% of the width of the patterned area). More uniform large area patterning can be realized by a proper beam shaping, allowing a uniform intensity profile.[24]

These results are expected to be immediately applicable in a number of experiments involving functional substrates for photonic, optoelectronic and biological applications, high-resolution lithography, and microfluidic devices.

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