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# Real-time near-field imaging of photoinduced matter motion in thin solid films containing azobenzene derivatives

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We present a study of the formation of surface relief gratings in thin solid films containing azobenzene derivatives upon illumination with an interference pattern. This study is based on near-field microscopy techniques that provide real-time imaging of both the photomechanical response of the material and light excitation profile. We demonstrate that the material deformation follows two distinct regimes characterized by different kinetics, a different phase relative to the light intensity pattern, and a specific dependence on light polarization. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073742]

Several spectacular photomechanical processes directly driven by the photoisomerization transition of azobenzene molecules have been discovered in recent years.<sup>1–8</sup> The conformation change between *trans* and *cis* states that undergoes an azobenzene molecule upon photon absorption produces a mechanical work, which is at the origin of various matter deformation and mass transport phenomena occurring at different scales from the nanometer up to the millimeter range. In particular, in thin solid films containing azobenzene derivatives bound to a polymer backbone, efficient matter migration occurs upon light illumination in the visible absorption band of the chromophores, leading to the formation of surface relief patterns.<sup>1,2</sup> Intriguing aspects of this phenomenon raised debated questions. In particular, the efficiency and directionality of the matter motion have been found to strongly depend on the light electric field orientation giving rise to a variety of photoinduced pattern shapes depending on the illumination conditions.<sup>4,7,9–12</sup> Several studies of the kinetics of the deformation process have been performed as a function of light polarization. These studies are mainly based on the measurement versus exposure time of the diffraction efficiency of the surface relief grating (SRG) that forms in an azopolymer film upon projection of an interference pattern.<sup>9,13–15</sup> However, the interpretation of the observed phenomena is a very intricate problem, which is still unsolved in spite of many theoretical attempts, probably because several microscopic mechanisms are in fact involved in the photoinduced deformation processes.<sup>16</sup>

In this letter, we present a study of the photoinduced SRG formation in an azobenzene-containing thin film, which unambiguously demonstrates that at least two distinct microscopic mechanisms are at the origin of the SRG formation. This study is based on near-field techniques that allow to image simultaneously *in situ* and in real time both the exciting light interference pattern and the surface topography.<sup>17</sup> As a result, we evidenced a transition between two subsequent photoinduced SRG formation regimes, which have completely different characteristics in terms of phase relative to the light profile, time scale, relief amplitude, and dependence on light polarization. Tuning light polarization allows to isolate one mechanism relative to the other and thus to follow both processes independently.

The experiments have been performed on a 450-nm-thick sol-gel photochromic film, the synthesis of which has been previously reported in detail.<sup>4,18</sup> Functionalized monomers bearing dispersed red 1 (DR1) azobenzene derivatives are grafted to the silica matrix so that to achieve a dye concentration of about 1 molecule/nm<sup>3</sup>. The *trans-cis* photoisomerization transition of the DR1 moieties is achieved by illumination in its visible absorption band. The presence of electron donor/electron acceptor substituents in the DR1 ensures an efficient *cis*→*trans* back reaction either by thermal activation or by photon absorption. The film was deposited on a glass substrate by spin coating. The sample was not thermally treated in order to obtain a weakly cross linked silica network, which does not impede the mobility of the photoactive molecules.

In our experiment [Fig. 1(a)], an interference pattern is produced by two laser beams with an average power density of 200 mW/cm<sup>2</sup>. Under these conditions thermal effects are negligible. The light wavelength is  $\lambda=473$  nm and the incident angle is  $\theta\approx 16.5^\circ$ . This yields an interference spatial period  $\lambda/(2\sin\theta)=\pi/k_x\approx 830$  nm ( $k_x$  being the in-plane wave vector component). This interference pattern is projected from the back side of the sample through the substrate. On the front side, the single-mode optical fiber tip of a combined shear-force and near-field optical microscope<sup>4,17</sup> is used to achieve simultaneous imaging of the surface topography and of the transmitted light intensity  $I$ . The measured light intensity profile  $I/I_0=2[1+A\cos(2k_x x)]$  ( $I_0$  being the transmitted intensity for a single incident beam) exhibits a contrast  $A$ , which value depends on the polarization of the beams. The experimental values of  $A$  are close to the calculated values [see for instance Fig. 1(b)], which indicates a lateral optical resolution better than 100 nm.<sup>19</sup>

Figure 1(c) shows the evolution of the surface topography of the film recorded simultaneously to the interference pattern of Fig. 1(b), which is produced by two *p*-polarized laser beams. These 256×256 pixel images are acquired with a 1 Hz *x*-scan rate. Thus, variations observed along the slow-scan direction of Fig. 1(c) (*y* axis) represent the topography evolution over 256 s with 1 s steps. The initial surface (at the bottom of the image) is flat exhibiting a typical roughness of 1 nm. When the laser is turned on, a sinusoidal SRG takes shape immediately. This SRG is *in phase* with the light intensity profile, which is opposite to all the previous obser-

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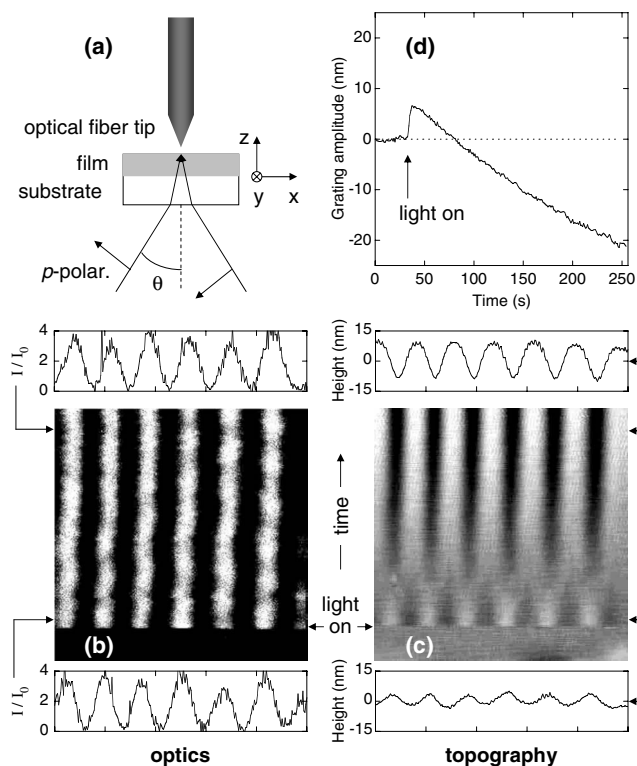


FIG. 1. *In situ* and real-time measurement of the deformation induced by two *p*-polarized interfering laser beams in a 450-nm-thick sol-gel film. (a) Experimental setup. (b)  $5 \times 5 \mu\text{m}^2$  optical image of the interference pattern at the sample surface. Intensity profiles at 10 and 200 s exposure times are plotted. The measured value of the contrast is close to the calculated value  $A \approx 0.93$ . (c)  $5 \times 5 \mu\text{m}^2$  surface topography image acquired during illumination. Topography profiles at 10 and 200 s exposure times are plotted. (d) Variation vs exposure time of the amplitude of the photoinduced SRG.

variations in similar conditions. Note that, for different light power densities ranging from 30 to  $800 \text{ mW cm}^{-2}$ , we have observed the same behavior with a deformation rate scaling linearly with the power density, which excludes any thermal effects. The SRG amplitude reaches a maximum value of about 7 nm after only 3 s exposure and then vanishes steadily. Subsequently, another grating starts to appear at the rate of about  $0.20 \text{ nm/s}$ , but it builds up with a spatial phase opposite to that of the interference pattern. The kinetics of the surface relief formation plotted in Fig. 1(d) is obtained from the difference between the topography profiles along bright and dark interference fringes. It exhibits a sharp onset and then a constant decrease with a sign change that indicates the  $\pi$ -type phase shift with respect to the interference pattern at the transition between the two SRG formation regimes. When changing light polarization (Fig. 2), i.e., illuminating the film with *s*-polarized interfering beams, only one deformation regime is observed. A grating indeed forms in phase relative with the optical excitation. The onset is similar to the first deformation regime observed with *p*-polarized illumination except that, after a few seconds, the grating amplitude saturates at a value of about 9 nm and only a very slight decrease is subsequently observed. These results clearly demonstrate that two distinct mechanisms produce photoinduced relief patterns in azobenzene containing thin films. The matter migration, which is generally reported, corresponds to the second regime observed in Fig. 1(c). It is efficient with *p*-polarized light excitation and almost completely inhibited with *s*-polarized light excitation. It produces a relief in the opposite phase relative to the light pattern.

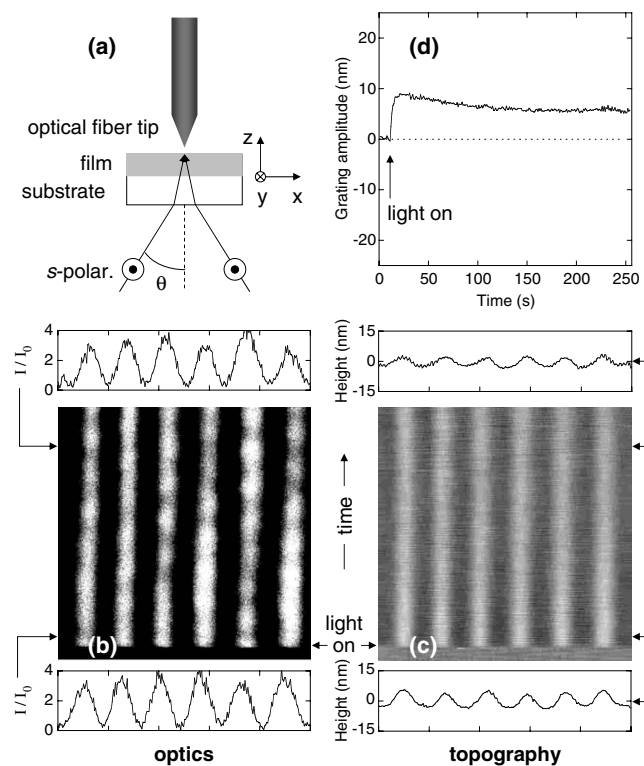


FIG. 2. Same as Fig. 1 except that the interference pattern is produced by two *s*-polarized incident laser beams. The contrast of the measured interference profile (b) is close to the calculated value  $A = 1$ .

Finally, it occurs at a relatively slow rate, since mass transport over distances much larger than the molecule size requires many photoisomerization events. In contrast, the first stage of the surface deformation is obtained with intensity interference pattern, which is produced by either *s*- or *p*-polarized beams. It takes shape in-phase with the interference pattern. It occurs on the time scale of only a few photoisomerization cycles since the average rate of isomerization cycling of a molecule is easily estimated to be of the order of 1 cycle/s in our conditions. This deformation regime can be interpreted as a photoexpansion of the material resulting from the azobenzene molecule photoisomerization. Indeed, the isomerization of an azobenzene unit requires a free volume of about  $0.127 \text{ nm}^3$ .<sup>20</sup> In sol-gel silica matrices it can be estimated that, on average, only 65%–85% of this free volume is available.<sup>21</sup> Since the azobenzene concentration in the material is 1 molecule/ $\text{nm}^3$ , a free volume equivalent to 2%–5% of the whole material volume is missing that would allow free isomerization of all the azobenzene molecules. We may thus assume that molecule photoisomerization induces a stress in the material, which is relaxed by a rearrangement of the matrix. This rearrangement leads to an increase in the film thickness, which gives rise to the formation of a SRG in phase with light intensity profile. Since this matrix rearrangement is local, it is completed over the whole film thickness within a few isomerization cycles, i.e., on a very short time scale. The amplitude of the SRG that we observed with *s*-polarized light is 9 nm, which corresponds to 5% of the film thickness and is thus consistent with the above estimation of the missing free volume fraction. Photoexpansion with similar amplitude and time scale has already been detected by ellipsometry measurements in azopolymer films.<sup>22</sup> Our measurements provide direct evidence that this photoexpansion process may produce the very fast formation of

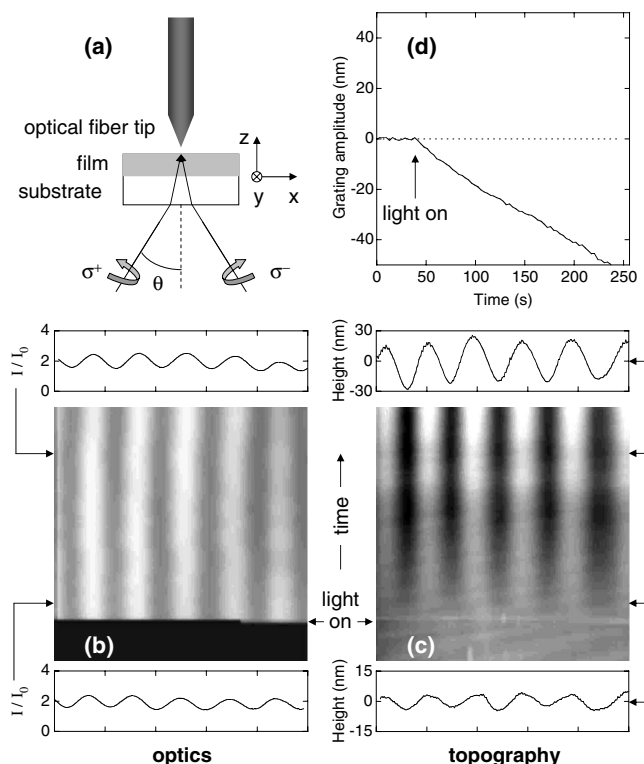


FIG. 3. Same as Fig. 2 except that two counter-rotating circularly polarized beams are used to produce a polarization interference pattern. The 15% contrast in the optical image (b) is mainly due to the anisotropy of the tip collection efficiency.

SRG. The interpretation in terms of photoexpansion implies that the fast SRG formation should not appear with *polarization* interference pattern of constant light intensity. Such a configuration is obtained by combining right-left circularly polarized beams.<sup>9</sup> As shown in Fig. 3, the local short-time SRG formation does not occur in this case and only the formation of a SRG with the characteristics of the matter migration takes place. As expected, in this illumination configuration, photoexpansion is spatially homogeneous over the film plane and does not yield any deformation.

In conclusion, we report the real time near-field imaging of the photoinduced SRG formation in thin sol-gel films containing azobenzene molecules. We show that, when using intensity interference pattern, a photoinduced SRG builds up on a short time scale, in the spatial phase with the optical excitation. With *p*-polarization, which addresses molecules oriented along the light pattern gradient, photoinduced matter migration occurs from bright to dark areas, erases the initial deformation, and leaves an out-of-phase SRG. With *s*-polarization, which addresses molecules oriented along the fringes, the photoinduced mass transport is inhibited and the initial SRG remains. We attribute this initial deformation to the photoexpansion of the bulk material resulting from the relaxation of the internal stress induced by the molecule photoisomerization. The stress relaxation is achieved by the sudden rearrangement of silica chains located in the illuminated areas. These results provide additional inputs in the debate on the photomechanical properties in azopolymer materials.<sup>7,23,24</sup> In particular, since both *s*- and *p*-linear polarizations yield the same SRG onset due to photoexpansion, it is unlikely that the internal pressure induced by the molecule photoisomerization is directly responsible for the

very polarization-dependent matter migration as proposed previously.<sup>14</sup> Moreover, a short time process at the initial state of SRG formation has been reported on the basis of diffraction measurements and interpreted in terms of “density” grating.<sup>15</sup> However, this process was observed upon illumination with a *polarization* interference pattern and thus cannot be consistently explained by the short time photoexpansion process, which here produces SRG only with *intensity* interference pattern. Finally, let us emphasize that upon illumination with counter-circularly polarized beams, the efficiency of the photoinduced matter migration is highly increased [Fig. 3(d)] with respect to *p*-polarized interference excitation [Fig. 1(d)], as already reported.<sup>9</sup> We suggest that photoexpansion might favor the matrix mobility. Thus, since photoexpansion is produced uniformly over the film plane with polarization interference pattern, it might contribute to reinforcement of the SRG formation efficiency.

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