Longitudinal anisotropy of the photoinduced molecular migration in azobenzene polymer films

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The effects of tightly focused, higher-order laser beams on the photoinduced molecular migration and surface deformations in azobenzene polymer films are investigated. We demonstrate that the surface relief is principally triggered by longitudinal fields, i.e., electric fields polarized along the optical axis of the focused beam. Our findings can be explained by the translational diffusion of isomerized chromophores when the constraining effect of the polymer–air interface is considered. © 2006 Optical Society of America

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Photoinduced mass transport in thin polymer films containing azobenzene chromophores have been extensively studied for their applications in optical data storage,[1,2] self-developing functional optical elements,[3,4] and optical near-field investigations.[5,6] Surface relief is the result of large-scale migration of the polymer backbone caused by the repetitive cycling of *trans–cis* photoisomerization of the aromatic group.[7] It was found that a variation of the spatial distribution of the light intensity involving lateral field components was necessary to optically induce surface modulation.[8,9] In this work, we experimentally demonstrate that the deformation of the polymer surface is extremely sensitive to inhomogeneous optical fields produced by the tight focusing of higher-order laser beams. In particular, we show that the surface profile reproduces the intensity distribution of longitudinal fields created in the focal regions.

Our studies were conducted on thin films of azoaromatic Disperse Red 1 (DR1) chromophores covalently grafted to a polymethylmethacrylate (PMMA) matrix. DR1 is characterized by a reversible *trans*-to-*cis* photoisomerization process. The compound was dissolved in 1,1,2-trichloroethane with a concentration of 25 g/l for 48 h under constant agitation. 40 nm thick films were produced by spin casting a 5 μl solution at 3000 rpm/s on a glass substrate. We used an excitation wavelength of 532 nm that is close to the absorption maximum of the dye. We used high-order laser beams focused to a diffraction-limited region to study the modification of the polymer surface. The peculiarity of these beams is that they produce inhomogeneous optical-field distributions in the focal region.[10] In particular, the field distribution is no longer purely transverse, and near the focus the field vectors can have strong components in the direction of propagation.[11–13] In the context of the present work, inhomogeneous field distribution provides a suitable basis to test the various migration models.[14] In our experiments, the original fundamental Gaussian mode HG_{00} of the laser beam was mode converted to produce a Hermite–Gaussian HG_{10} mode and radially and azimuthally polarized Laguerre–Gaussian beams by using an arrangement of retarder plates.[12] A high-numerical-aperture (NA) oil-immersion lens ($60\times$, 1.4 NA) ensured the tight focusing of the laser beams. The photomodification of the polymer was subsequently observed by atomic force microscopy (AFM).

Figures 1(a) and 1(b) show topographic images of the deformation of the surface induced by a focused

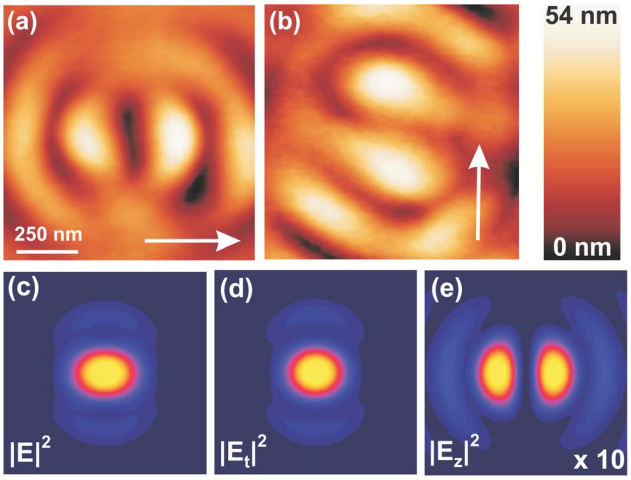

Fig. 1. (Color online) (a), (b) Topography of the photoinduced deformation of a tightly focused HG_{00} beam polarized horizontally and vertically, respectively. (c) Calculated total intensity distribution $|E|^2$ inside the focal region of a HG_{00} mode polarized horizontally. Decomposition of $|E|^2$ in (d) transverse $|E_t|^2$ and (e) longitudinal components $|E_z|^2$. Linear color scaling; image sizes 1 μm.

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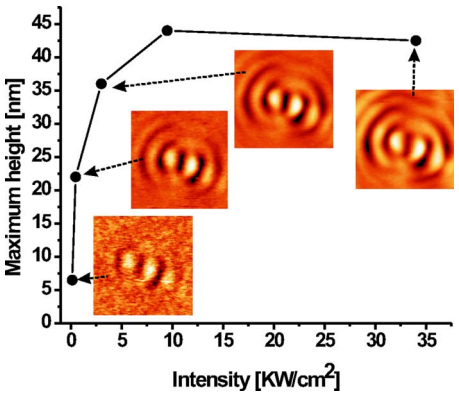

Fig. 2. (Color online) Maximum height deformation of the surface for increasing laser intensity. The images represent the corresponding topographies (image size 1.5 μm).

HG_{00} beam for two orthogonal polarizations. The polymer was exposed to the focused laser beam for 1 s at an estimated intensity of 40 kW/cm^2. To understand the origin of the reorganization of the polymer inside a focused HG_{00} beam, we calculated the focal intensity distribution. We used the multiple-multipole (MMP) approach[15] to evaluate the square modulus of the electric field $|E|^2$ in a plane 5 nm below the polymer surface, using the experimental parameters. The field distribution was not modified across the thickness of the thin PMMA layer. Figure 1(c) simulates the total intensity distribution inside the focus for a horizontal polarization. Because of the breakdown of the paraxial approximation in tight focuses, the total intensity $|E|^2$ can be decomposed as a linear superposition of a transverse component of the intensity $|E_t|^2=|E_x|^2+|E_y|^2$ and a longitudinal component $|E_z|^2$ as shown in Figs. 1(d) and 1(e). Note that the magnitude of $|E_z|^2$ is ten times weaker than $|E_t|^2$.

The experimental patterns are different from the ones reported in the literature for weakly focused linearly polarized Gaussian beams.[9] The polymer was observed to move away from the region of higher intensity, producing a pronounced spherical dip on the surface. The profile of the depletion was correlated with the lateral intensity distribution. After reorganization, the displaced polymer accumulated along the polarization direction on the sides of the large central depletion. Figures 1(a) and 1(b) cannot be explained by lateral diffusion of the polymer triggered by transverse components where a central depletion qualitatively similar to the spatial distribution of $|E_t|^2$ [Fig. 1(d)] would be expected. Instead, we observed a narrow crevice at the center of the focus surrounded by two elevated lobes separated along the polarization direction. Interestingly, the photoinduced pattern replicates the calculated longitudinal component of Fig. 1(e), where elevated regions are correlated with locations of large $|E_z|^2$.

Bian *et al.* observed that, under high intensities, peaklike deformations appeared as the result of a photobleaching of the complex.[9] The location of the peak coincided with the maximum intensity of their illumination. This effect was simultaneously observed with an increase of the low-intensity surface deformation, allowing a clear distinction between the different responses of the complex. Our excitation intensity is typically an order of magnitude more intense than previous studies[14] and is the result of the extreme focusing of the beam and the short exposure time. We investigated the deformation of the surface as a function of excitation intensity in order to discriminate the effect of chemical decomposition in the interpretation of the deformation. Figure 2 shows the relative height of one of the central lobes for increasing laser intensities. The lobe height increases with laser intensity and reaches a plateau at approximately 40 nm due to the limited amount of polymer within and near the focal volume. The topographic images essentially show the same two-lobe pattern even at low intensity, where the induced modification is only a few nanometers high. This behavior differs from the photobleaching mode, where the shapes of the photoinduced patterns are intensity dependent.[9] The fact that the lateral distance between the two lobes is constant regardless of the intensity indicates that polymer migration does not originate from a lateral diffusion and that, although ten times weaker than $|E_t|^2$, $|E_z|^2$ plays the dominant role in the surface modification.

We then tested the sensitivity of reorganization when illuminated with higher-order laser modes, known to produce various spatial distributions of longitudinal fields. Figures 3(a)–3(c) show the intensity distribution of $|E|^2$ for a focused Hermite–Gaussian HG_{10} beam and its decomposition into the in-plane $|E_t|^2$ and out-of-plane $|E_z|^2$ components, respectively. $|E_z|^2$ is now composed of three maxima oriented with the polarization direction.[10,13] The experimental pattern is shown in Fig. 3(d) and is composed of three elongated lobes that strongly correlate with $|E_z|^2$. The calculated $|E|^2$ distribution of a focused radial mode and its decomposition into $|E_t|^2$ and $|E_z|^2$ are shown in Figs. 3(e)–3(g). The magnitude of $|E_z|^2$ exceeds by a factor of 3 the transverse component, with most of the intensity located in a circularly symmetric cen-

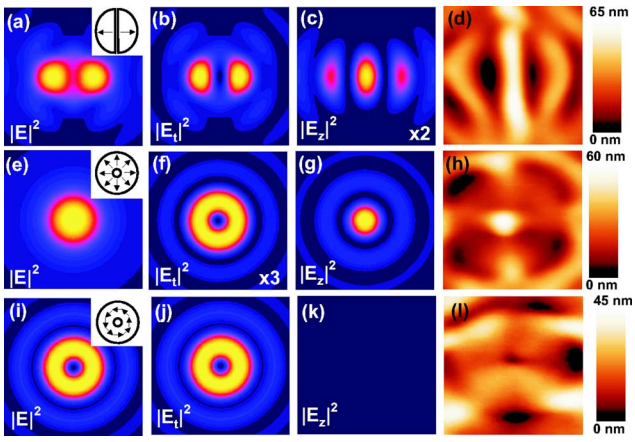

Fig. 3. (Color online) Field distribution and photoinduced pattern inside the focal region of a Hermite–Gaussian HG_{10} (row 1), radial (row 2), and azimuthal (row 3) beam. The mode profiles and polarization vectors are displayed in the insets. First column, total intensities $|E|^2$. Second column, transverse intensities $|E_t|^2$. Third column, longitudinal intensities $|E_z|^2$. Fourth column, resulting surface topographies. Image size 1 μm.

tral region. Figure 3(h) shows the resulting surface after irradiation. Similar to the HG_{00} and HG_{10} excitations, the pattern strongly resembles the $|E_z|^2$ distribution with a central peak (full width at half-maximum is approximately 100 nm) surrounded by a valley. The fourfold symmetry seen in the topography originates from the wave plate cross arrangements used to produce the radial mode. It is interesting to note that the central peak must originate from an additive effect of the photoinduced migration due to $|E_z|^2$ and $|E_t|^2$. The radially symmetric lateral motion of the polymer would result in a buildup at the center. However, it is reasonable to assume that the effect of $|E_t|^2$ on the central peak must be weak if we take into account the magnitude of $|E_z|^2$ compared with $|E_t|^2$ and the large z-field sensitivity revealed by Fig. 1. Finally, we investigated the deformation due to a focused azimuthal illumination where there are no polarization vectors aligned with a gradient of intensity. The symmetry of the polarization vectors prevents the formation of any fields axially oriented, as shown in Figs. 3(i)–3(k). $|E|^2$ is exclusively composed of transverse fields. Figure 3(l) shows the topography of the polymer after irradiation with such a mode. The polymer response does not produce elevated regions within the focal area as opposed to the other modes. Instead, a small depletion is created in the center that is surrounded by an area with relatively low surface modulation. These features are intuitively expected from a vortex-driven viscous flow.

The different models developed so far suggest that surface deformation is produced by confined regions of intensity along a transverse polarization vector.[8,9,14,16] However, the generally accepted optical-field gradient force model[9] also predicts the surface profile to resemble the second derivative of the intensity, which is not observed in our case. Perhaps most important, the gradient force model does not provide an explanation for the large sensitivity of the photoinduced process to optical fields oriented longitudinally. Lefin *et al.* recently proposed an alternative mechanism. The essential feature of their model is that chromophores undergoing repetitive *trans–cis–trans* cycles also experience translational diffusion in a direction defined by the electric field vector.[16] In the context of this model, it is reasonable to assume that the viscoelastic forces generated by the molecular diffusion of the dye are considerably larger for an in-plane motion than for a direction normal to the surface. For the case of a thin film, interface discontinuities (glass–polymer–air) are present, and free-space volumes need to be taken into account. Considering the above assumption, the diffusion model can explain the sensitivity to the longitudinal intensity distributions. The inhomogeneous polarization in the focus triggers in-plane and out-of-plane translational diffusions, and the surface deformation simply reflects the energetically favorable direction. The longitudinal anisotropy revealed here offers an element of explanation for the origin of the nanometer scale photoinduced surface reorganization observed in recent optical near-field experiments based on localized electromagnetic enhancement.[5]

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