Probing optical near-fields with photoreactive azo-polymers

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Abstract. In this work, we demonstrate a method to visualize optical near-fields on photosensitive azo-polymer thin films with scanning near-field optical microscopy. A near-field intensity profile is determined in a basis of surface deformations of the azo-polymer thin film exposed to linearly polarized light.

1. Introduction
One of the most important issues in modern photonics and spectroscopy is the control and evaluation of the polarization state of optical near-fields. A control of the near-field polarization allows one to manipulate the light beyond the Abbe’s diffraction limit. This is mainly used in non-volatile data storage and molecular switching [1, 2, 3, 4].

Besides, the near-field polarization plays a critical role in different optical techniques, such as scanning near-field microscopy (SNOM/NSOM) and tip-enhanced Raman spectroscopy (TERS) [5]. The control of near-field polarization enables to perform single-molecule sensitive experiments [6], to probe longitudinal and transverse optical anisotropy [7], and to determine the spatial orientation of molecules, and their symmetry. Also, it allows one to improve the spatial resolution in optical microscopy and spectroscopy [8]. The monitoring of the near-field enriches 3D polarized Raman microscopy [9, 10, 11] and near-field fluorescent microscopy [12].

The polarization of the light has a significant effect on the intensity distribution in the light beam. Due to the deformations of the polymer under the influence of incident light, we can observe the intensity profile of a polarized beam. This approach is valid both for far-fields and near-fields of the light.

In this paper, we demonstrate a method for visualization of the polarized optical near-fields on photosensitive azo-polymer thin films for the scanning near-field optical microscopy.

2. Experimental
In order to study the polarization of the near-field aperture probe, we realized a scheme of a scanning near-field microscope in transmission geometry based on a scanning probe microscope equipped with a confocal optical spectrometer NTEGRA Spectra (NT-MTD) (SNOM, figure 1). A commercial probe (NT-MTD) was taken as a test of the aperture of the probe. We applied photosensitive films a side-chain 4-amino-4-nitroazobenzene chromophore covalently attached to the polymer backbone of two epoxy-based oligomers containing hydroxyl groups (CFAO) Films were prepared by dissolving 7% wt CFAO compound in 1 mL cyclohexanone. A CFAO thin film was produced by spin coating 5 μl CFAO solution, in addition diluted by 10 times with cyclohexanone, onto an ITO/glass substrate at
3 000 rpm for 3 min, followed by annealing at the glass transition temperature of $T_g = 130^\circ$C and 10 mbar for 1 h in order to remove solvent remains. We used this sample, due to its visible absorption spectrum with a maximal intensity peaked at 490 nm.

**Figure 1.** a) The mechanism of producing surface deformations by high-order Gaussian beams and b) the experimental setup of SNOM.

To control the spatial resolution of our setup, we used a standard optical grid (SN01, NT-MTD) for near-field measurements. Figure 2 represents lateral-force microscopy (A), confocal microscopy (B), and scanning near field microscopy (C) images of the optical grid SN01. On these data we can conclude, that near-field optical spatial resolution of this experimental setup amounts to 100 nm.

**Figure 2.** Lateral-force microscopy imaging (A), confocal (B) and near field (C) imaging of standard optical grid. Spatial resolution ~ 100nm.

We conducted a concomitant experiment on the deformation of the azo-polymers by incident light. In our experiment, we study photo-induced deformation of CFAO films produced by focused high-order Gaussian beams. A 633 nm He-Ne laser beam is focused into a spot of 200 nm in diameter using an 100x objective with numerical aperture NA=1.49. We use a half-wave S-waveplate to produce the radial- and azimuthal- polarized laser beams (ALTECHNA). Also, we did the experiment for linear polarized Gaussian beams. We used a hybrid SPM-equipped Raman spectrometer (NTEGRA SPECTRA, NT-MDT) was used to make topographic images of surface deformations. To produce the surface deformations on the CFAO thin film, the time exposure was 1 min.
3. Theoretical background

Azopolymers undergo photoisomerisation under the incident light. The consequence of this phenomenon is motions of the chromophores. There are three types of motions in azopolymers: the first one is chromophores motions, which is caused by polarization of the incident light. As for linearly polarized light, the photoisomerisation is activated by the chromophore’s transition dipole moment axis has a component parallel to the light polarization. The second type is the ‘domain’ motion. It requires the bounds between chromophores and the polymer matrix. The last type of motion appears on macroscopic scale, which reason is pressure gradient, [13, 14].

Bian et al first discovered the photo-induced deformation of azopolymer by means of focused Gaussian beams [15, 16, 17, 18]. In the polarizable azopolymer film an optical electric field \( E(\mathbf{r}, t) \) induces a polarization \( \mathbf{P}(\mathbf{r}, t) = \varepsilon_0 \chi \mathbf{E}(\mathbf{r}, t) \), where \( \varepsilon_0 \) is the permittivity of vacuum and \( \chi \) is the medium susceptibility. The time averaged force density exerted on azochromophores in a small volume is represented by:

\[
\mathbf{f}(\mathbf{r}) = \langle \mathbf{P}(\mathbf{r}, t) \times \nabla, \mathbf{E}(\mathbf{r}, t) \rangle,
\]

where \( \mathbf{P}(\mathbf{r}, t) \) is the film polarizability.

The field deforms azopolymers according to the law:

\[
S(x, y, t) = \frac{1}{4} h \mu \varepsilon_0 \chi' \int_0^T \mathbf{v}_s \times \mathbf{f}_{z=0} dt
\]

where \( h \) is thickness of the polymer, \( \mu \) is the proportionality factor that depends on the viscosity and form of polymeric chains, \( \varepsilon_0 \) is the permittivity in vacuum, \( \chi' \) is real part of the susceptibility of the polymer, \( T \) is time exposure, \( \mathbf{f} \) is force, that deforms polymer.

4. Results and discussions

In our work we applied this theoretical description of deformations [17, 18] and used it for our mathematical modeling of radial- and azimuthal-polarized Gaussian beams. Furthermore, mathematical modeling of radial- and azimuthal-polarized light was performed using the Jones matrix method. As a result, we gained calculation for linear, radial and azimuthal polarizations for Gaussian beams.

![Figure 3. Calculations of surface deformation produced by linear (A, B), azimuthal (C) and radial (D) polarized Gaussian beams. AFM images of surface deformation produced by linear (E, F), azimuthal (G) and radial (H) polarized Gaussian beams.](image)

The visualization of near and far fields has been achieved with photo-induced surface deformations. For linear, radial and azimuthal polarization, we obtain AFM images of surface
deformations (Figure 3 (E), (F), (G), (H)). In figure 3 (E-H), the distribution corresponds to the dark areas of maximum light intensity, while the maximum surface deformations arise in the maxima gradient of the optical field.

By using the photo induced deformations method, we receive the near-field intensity profile for the aperture probe in scanning near-field microscopy (figure 4). A near-field intensity profile is determined on the basis of surface deformations of the azo-polymer thin film exposed to linearly polarized light. In figure 4, dark areas correspond to a maximum intensity of the optical near–field.

5. Conclusion
We demonstrate a visualization technique for near field light in scanning near field microscopy by using photosensitive azo-polymer films. In summary, we conclude that the direction of linear polarization changes during the propagation in the optical fiber and localization process in SNOM tip.

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