Near-field optical research on the Azobenzene Polymer Films

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ABSTRACT

We report the near-field investigation on azobenzene contained polymer films using scanning near-field optical microscopy. Nanometer scale dots and lines were inscribed on these films, and the topographies and transmitting images of these patterns could be obtained at the same time. The transmitting images were in agreements with the topographies, and it proved that trans-cis isomerization of the azobenzene moieties in the illuminated area induced both surface relief and anisotropy. The experimental results helped to discover the mechanism of the photo induced surface relief and anisotropy, and the agreement between the transmitting images and the topographies could be applied in pure optical writing/reading in high-density data storage.

Keywords: Scanning near field optical microscopy, Azobenzene polymer films, photoinduced anisotropy, surface deformation.

1. Introduction

Azobenzene and its derivatives have attracted much interest in the past few years because of a numbers of fascinating features of these compounds. Such as photo induced optical anisotropy (POA), which can be detected in dichroism and birefringence measurements, and photo induced surface relief, which can be detected by Atomic force microscopy. When irradiated with polarized light two phenomena happened simultaneously. Now many theories were proposed to illustrate these two phenomena individually, and seldom linked them together, especially in nanometer scale area. Near-field scanning microscopy (NSOM) is a good instrument for investigated nanometer scale area phenomena, such as detecting fluoresce of single molecule, trapping and manipulation of nano-objects, and also inscribing patterns of subwavelength scale, and so on. In our experiment, nanometer scale patterns were inscribed on the polymer films by the near-field method, and both the surface relief and anisotropy can be observed at the same time, which helped to understand the mechanism of the photo induced surface relief and anisotropy, and showed potential for future pure optical writing/reading in high-density data storage.

2. Experiment:

The photosensitive materials using in this experiment was poly-[2-(4-(4-cyanophenyl) phenoxy) ethoxyl methaetylate] (CN2), which contains a common azobenzene moiety in the side-chain. The thin films were prepared by casting dilute solutions of the azo-polymer in tetrahydrofuran onto freshly cleaned glass substrates and the solvent was then removed. The glass transition temperature $T_g$ of these films is 393K. The absorption

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The spectrum of the azobenzene polymer films was shown in Fig. 1. The experiment set-up is shown in Fig. 2. The scanning stage of this SNOM is Nanonics100, and the controlling system is the product of RHK Technology Inc. The SNOM was working in contact mode and the distance between the tip and the films could be controlled at about 10nm. Ar+ laser at 457nm illuminated the sample via the Nanonics Cantilevered aperture optical probe whose aperture diameter is about 100nm. When the probe fell about several nanometers above the surface of the films, the light from the tip illuminated the films at fixed points for about ten seconds. As a result, four dots were inscribed on the films as shown in Fig. 3. At the same way, when the probe with laser scanned along the Y-axis back and forth at a fixed value on X-axis for about one minutes, a line was then inscribed on the film, and changed the X value and repeated the same process, we could obtained another two lines as shown in Fig. 4. After the processes of inscribing, we weakened the intensity of the laser greatly so that during the following scanning the light from the probe would not induce isomerization again. It was warranted by the following two reasons: First, the intensity of the laser was weakened, so it would not damaged the patterns inscribed before; second, the scanning speed was as fast as 7ms per line. In the process of scanning, the wavelength and polarization of detecting light remained the same as that of the inscribing light, for the reason that we wanted to investigate the reaction of the azobenzene contained polymers to a certain polarized light.

3. RESULTS AND DISCUSSION

Topographies and transmitting images were obtained at the same time as shown in Fig. 3 and Fig. 4. In Fig. 3 the left image was the topography of four dots inscribed and the right one was the corresponding transmitting images and the same for Fig. 4. In the Fig. 3 and Fig. 4, the transmitting images were in good agreement with corresponding topographies. In Fig. 3, the fringes of these dots were thicker than the center, but the intensity of transmitting light from fringe was larger than that from the center. This is because of the photoinduced anisotropy in the inscribed area.

Known to all, under illumination of polarized light, azobenzene moieties would undergo trans-cis isomerization and reorientation, and as a result, the illuminated area would function like a polarizer whose polarized direction was not parallel to that of the illuminating light.\(^\text{[10]}\) In our experiments the Ar ion laser at 457nm illuminated the films; photoinduced isomeration caused both the patterns and anisotropy. For dots in Fig. 3 the centers were just under the tip and after illumination they had the property of a polarizer. The polarization of the detecting light was the same as that of the inscribing light, so the intensity of transmitting light from the centers was smaller than that from fringes. For lines in Fig. 4 the corresponding relation between the two images was the same as that of dots in Fig. 3.

On another point, in Fig. 3 and Fig. 4 the transmitting images reappeared the topographies of these patterns very well, and it could be used in pure optical writing/reading in high-density data storage. Now much research on high-density data storage was just optical writing and topography reading. We can also change the wavelength of the detecting light which is out of the absorb region of the sample, and will not induced any isomeration. The related experiments will be carried out in future.

4. CONCLUSION

In this paper we investigated the optical property of the azobenzene contained polymer films using scanning near field optical microscopy. Both the topography and transmitting images were obtained at the same...
time. The comparison between the transmitting images and the topographies helped to understand photo induced surface relief and anisotropy of the azobenzene moieties. The experiment provided a method for future pure optical writing/reading in high-density data storage.

5. ACKNOWLEDGEMENTS

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6. REFERENCE

[7]: Betzig E., Chichester R. J., Lanni F., & Taylor D. L. Bioimaging, 1, 129 (1993)
Fig 1: U-V absorption spectrum of azobenzene polymer films and chemical structure of azobenzene polymer

![Absorbance spectrum and chemical structure of azobenzene polymer](image)

Fig 2: Schematic diagram of the experiment set-up.

- **FC**: Fiber coupler
- **PD**: Position detector
- **LD**: Laser diode

![Schematic diagram of the experiment set-up](image)

Fig 2: Schematic diagram of the experiment set-up. FC: fiber coupler, PD: position detector, LD: laser diode.
Fig 3: Dots inscribed by SNOM, left is topography, right transmitting image

Fig 4: Lines inscribed by SNOM, left is topography, right transmitting image