Near-field lithography on the azobenzene polymer liquid crystal films

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Received July 5, 2004

In this article, we reported near-field research on azobenzene polymer liquid crystal films using scanning near-field optical microscopy (SNOM). Optical writing and subsequently topographic reading of the patterns with subwavelength resolution were carried out in our experiments. Nanometer scale dots and lines were successfully fabricated on the films and the smallest dot diameter is about 120 nm. The width of the line fabricated is about 250 nm. This method is also a choice for nanolithography. The mechanism of the surface deformation on the polymer films was briefly analyzed from the viewpoint of gradient force in the optical near field. The intensity distribution of the electric field near the tip aperture was numerically simulated using finite-difference time-domain (FDTD) method and the numerical simulation results were consistent with the experimental results.

OCIS codes: 180.5810, 100.6640, 220.4610.

Scanning near-field optical microscopy (SNOM) has been widely used in physics, chemistry, and biological science because of its subwavelength resolution, nondestructive and real-time measurement[1−3]. For example, using SNOM, we can fabricate subwavelength optical elements (SOEs) , manipulate single atoms or molecules, and detect the fluorescence of many biological cells, etc.[3−5]. And now SOEs are under fast development because of their excellent features. One of the best techniques for fabricating SOEs is the nanoimprint lithography (NIL) developed by Professor Chou at Princeton University[6−8]. In this article we report nanometer scale lithography on azobenzene polymer using SNOM. Nanometer-scale dots and lines were fabricated. This method is also a choice for nanolithography.

The photosensitive materials used in this experiment is poly [2-(4-(4-cyanopheyl) phenyloxy) 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 this sample is about 393 K. The experiment set-up is shown in Fig. 1. The scanning stage of this SNOM/AFM (atomic force microscopy) is made by Nanonics Imaging Ltd., and the controlling system is the product of RHK Technology Inc.. Ar^+ laser at 454 nm illuminates the sample via the Nanonics cantilevered aperture optical probe. The diameter of the tip aperture in our experiment is about 100 nm. The SNOM/AFM is working in contact mode and the distance between the tip and the sample is about 10 nm. During the scanning we can obtain both the optical image and the topography image of the deformation simultaneously. The surface roughness of the sample before illumination was estimated by studying the topography image obtained with the SNOM/AFM. The room temperature was about 300 K.

If the wavelength of the laser lies in the region of the absorption spectrum[9], azo-polymer would absorb the light and optical cycling of the trans-cis-trans isomerization was induced. As a result, the orientation of the azo-dye molecules and the refraction index of the illuminated region change. The cycle is a necessary factor for the surface deformation and birefringence. This information can be stably stored below the glass transition temperature (T_g) of the polymer and can be erased by heating the azo-polymer above T_g. In our experiment the laser via tip aperture illuminated the films and the isomerization cycle along the direction of gradient force of the optical near field induced the mass migration.

We examined the influence of the near-field optical power on the dots shape by varying the illumination time. In Fig. 2, the three dots from left to right along the A

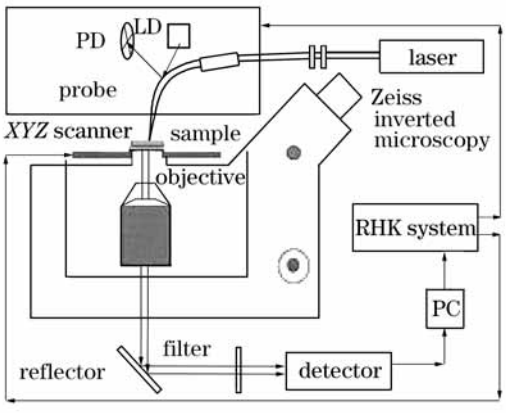

Fig. 1. Schematic diagram of the experiment set-up. FC: fiber coupler; PD: position detector; LD: laser diode.

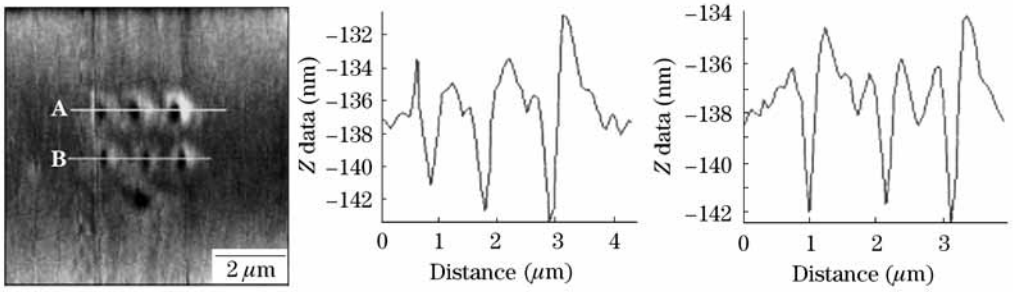

Fig. 2. The topography image of the azo-polymer after illumination and the profile analysis along the lines in the image.

line corresponding to the illumination time of 1, 2, 3 s, respectively. And the three dots along the B line were all illuminated for 1 s. From these, we can find the influence of the illumination time on the shape and size of these dots. The diameter and depth of the dots would enhance if the illumination time extended. In this experiment the minimum illumination time is 1 s for lack of good time control system. The minimum diameter (full width at half height) was about 120 nm, and smaller dot could be obtained also by decreasing the diameter of the tip aperture when the illumination time was constant. The minimum dot diameter which could be obtained by this methods would be larger than 50 nm. This is because that the minimum diameter of tip aperture is about 50 nm.

We can also find that the direction of the mass migration on the polymer surface was along the same direction. For comparison, the intensity distribution of the electric field near the tip aperture was calculated using the finite-difference time-domain (FDTD) method. The incident light was X-polarized Gaussian beam and propagated along the Z-axis. The calculated result was shown in Fig. 3. The shape of numerical simulation results was similar to the experimental results as shown in Fig. 2. Although there are some theories about the mechanism of the photo induced surface deformation on azobenzene polymer films[10,11], in this article we analyzed the calculated and experimental results and found that gradient force theory was the most suitable for explaining our experimental results. In Fig. 3, we found the intensity of the electric field on the edge of the tip aperture was larger than that in the center, so the gradient force of the optical field attracted the azobenzene molecule from the region with the weaker electric field towards the stronger fields. As a result, matter migration of the polymer took place, and these dots formed.

The principle of the gradient force is described as follows[12,13]. In a vacuum, dielectric materials are influenced by the optical electromagnetic field, so the materials receive a dynamic force. The optically induced gradient force density $f_{\rm d}$ is given as

$$\begin{cases} \widetilde{f}_{\rm d} = \langle [\widetilde{P}(\widetilde{r},t)\cdot\bigtriangledown]\widetilde{E}(\widetilde{r},t)\rangle \\ \widetilde{P}(\widetilde{r},t) = \varepsilon_0\chi\widetilde{E}(\widetilde{r},t) \end{cases}, \tag{1}$$

where $\langle\rangle$ stands for the time averaged process and $\widetilde{E}(r,t)$, $\widetilde{P}(r,t)$, ε_0, χ represent the optical field vector, the optically induced polarization vector, the permittivity of free space, and the susceptibility of the medium, respectively. Equation (1) implies that the polymer chains experience a force only when there is a component of optical field gradient along the polarization direction. The light from Ar^+ laser is X-polarized Gaussian beam whose optical field amplitude is described by $E(x) = E(0)\exp(-x^2/\omega^2)$, the force density, according to Eq. (1), is described by

$$f_{\rm d}(x) \propto \chi' {\rm d}I(x)/{\rm d}x, \tag{2}$$

where $I(x)$ is the intensity distribution of the Gaussian beam and χ' is the real part of the susceptibility. In this article, the intensity distribution of the electric field near the tip aperture was calculated and shown in Fig. 3. The direction of gradient force of the optical near field was along the X-axis deduced from Eqs. (1) and (2), so the direction of matter migration could be obtained, which was consistent with the experimental results.

We also draw lines on the films as shown in Fig. 4. In this situation, laser via the tip aperture scans along the Y-axis. The width of the line is about 250 nm. This

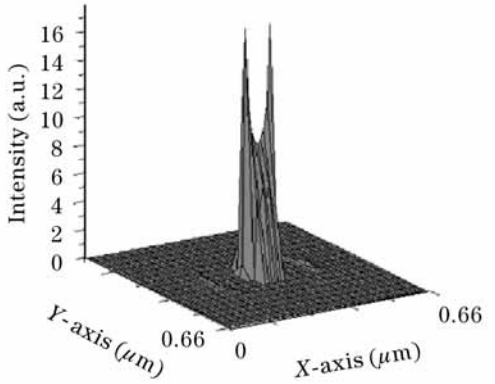

Fig. 3. The three-dimensional intensity distribution of the electric field near the probe aperture.

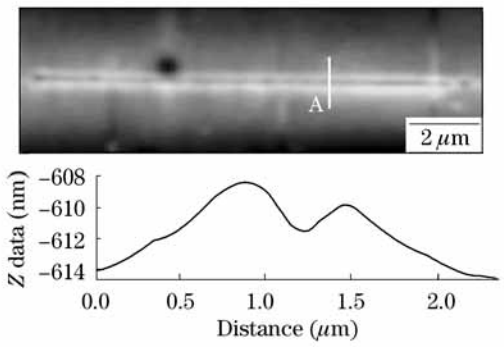

Fig. 4. Line (along Y-axis) fabricated by SNOM.

line can be used as waveguide that is useful in integrated optics. What is more, we can pattern many forms of subwavelength optical elements on the azobenzene polymer, such as grating, optical coupler, and so on. The related experiments are going on.

Nanometer scale dots and lines have been fabricated on the azobenzene polymer films by SNOM. The mechanism of the surface deformation on azobenzene polymer films was analyzed according to the gradient force theory, and the numerical simulation results were consistent with the experimental results. This method is feasible for fabricating subwavelength optical elements and these materials were proved to be suitable for fabrication.

This work was supported by the National Natural Science Foundation of China (No. 90206002), the National and Development Program of China (No. 2002AA313030), and the Provincial Natural Science Foundation of Anhui (No. 03046204). D. Zhang's e-mail address is dgzhang@ustc.edu, H. Ming's e-amil address is minghai@ustc.edu.cn.

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