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Fabrication of narrow surface relief features in a side-chain azobenzene polyester with a scanning near-field microscope

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Abstract

We show that it is possible to fabricate topographic submicron features in a side-chain azobenzene polyester with a scanning near-field optical microscope. Through irradiation at a wavelength of 488 nm at intensity levels of 12 W/cm^2, topographic features as narrow as 240 nm and as high as 6 nm have been reproducibly recorded in a thin film of the polyester. These observations are consistent with the fact that at low intensities peaks are produced evolving into formation of trenches at high intensities in the case of amorphous side-chain azobenzene polyesters. This may find applications in high-density optical storage and high-resolution lithography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Side-chain azobenzene; Near-field optical microscope; High-density optical storage; High-resolution lithography

It has been known for some years [1–3] that surface relief features arise when azobenzene-containing polymers are irradiated with polarized light. While making diffraction gratings with polarized beams, even orthogonally polarized beams have been found to give rise to strong surface features, concomitant to an anisotropic grating resulting from molecular realignment [4]. We have observed a displacement between the direction of polarization and the peak of the surface relief depending on the polymer architecture [5]. In order to confirm these results, light-induced surface changes in several azobenzene polyesters have been observed using three different techniques: (1) a diffraction analysis of polarization holographic gratings, (2) a transmission mask, and (3) single-focused beams. We have investigated polyesters that differ only in the nature of the substituent on the azobenzene [6]. We have shown that the behavior of the surface relief is dependent on the substituents. It is shown that the nature of the surface relief depends on the intensity of the irradiating beam. Both s- and p-polarized light have been found to produce surface relief.

Interest in azobenzene polymers has also arisen due to their potential for optical information storage. One of the questions that arises is the resolution capability in the polymers. Using a macroscopic optical arrangement, it is possible to achieve a resolution limited by the wavelength of light. Scanning near-field optical microscopy (SNOM) is an appropriate technology [7] for the investigation of the obtainable resolution and ultimate optical sensitivity in the polymers. Here we describe near-field optical lithographic experiments in a side-chain azobenzene polymer for the fabrication of surface relief features.

Our SNOM set-up has been built around a TopoMetrix Aurora near-field microscope that has been modified. An external lock-in amplifier (SR 850, Stanford Research Systems) is used to drive the feedback signal and extra external photomultipliers are used to detect the optical signal. A schematic drawing of the near-field set-up is shown in Fig. 1. From the initial experiments conducted with commercial near-field tips with a quoted tip size of 50 nm, it was not possible to induce either anisotropy or topographic changes in the polymer film. This is probably due to the very low transmission of the aperture, since the transmitted intensity is proportional to δ^4 where δ is the diameter of the aperture. In near-field microscopy, δ is much smaller than the wavelength of light. Using a Sutter Instruments P 2000 fiber puller, consisting of a CO_2 laser and a computer-controlled puller system, it has been possible to fabricate fiber tips from single-mode optical fibers (Spectron SMC A0630B) with almost flat ends with a diameter of 200 nm [8]. An

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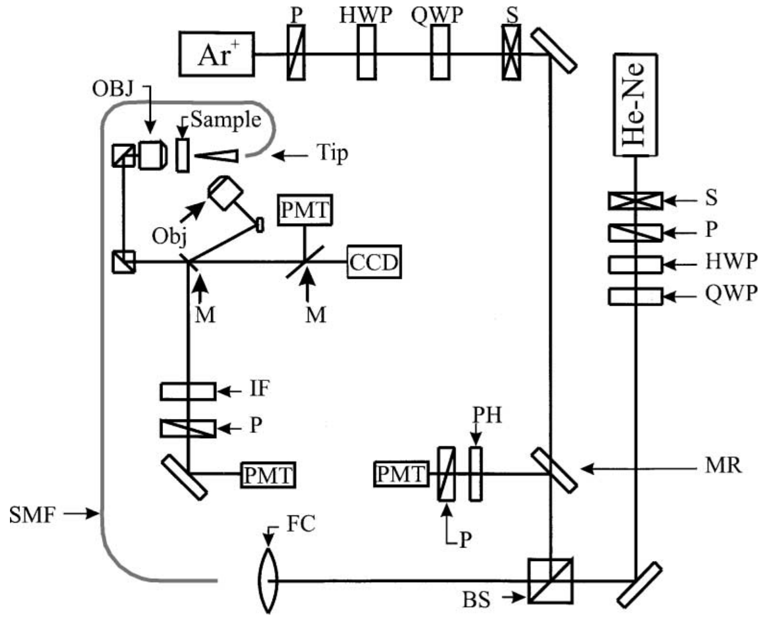

Fig. 1. Set-up for performing near-field lithography. In the figure, Ar^+ and He–Ne refer to argon and He–Ne lasers, respectively. S: shutters; P: polarizers; HWP: half-wave plates; QWP: quarter-wave plates; BS: beam-splitter; M: mirror; FC: fiber coupler; SMF: single-mode fiber; IF: interference filter; OBJ: microscope objective; PH: pin-hole; MR: mirror for reflection measurement; PMT: photomultiplier.

SEM image of the fiber tip is shown in Fig. 2. The tips are then coated with aluminum with a typical thickness of 100 nm. In order to be able to write in the polymer films and then read the result out, both an argon laser beam at 488 nm and a He–Ne laser beam at 633 nm can be coupled simultaneously into the optical fiber.

The polarization states of both beams are controlled by two sets of $\frac{1}{2}\lambda$ and $\frac{1}{4}\lambda$ waveplates to ensure that the light coming out of the near-field tip is linearly polarized with an angle of 45° between the polarization of the two laser beams. The two laser beams can be turned on and off independently by two shutters. The blue light from the argon

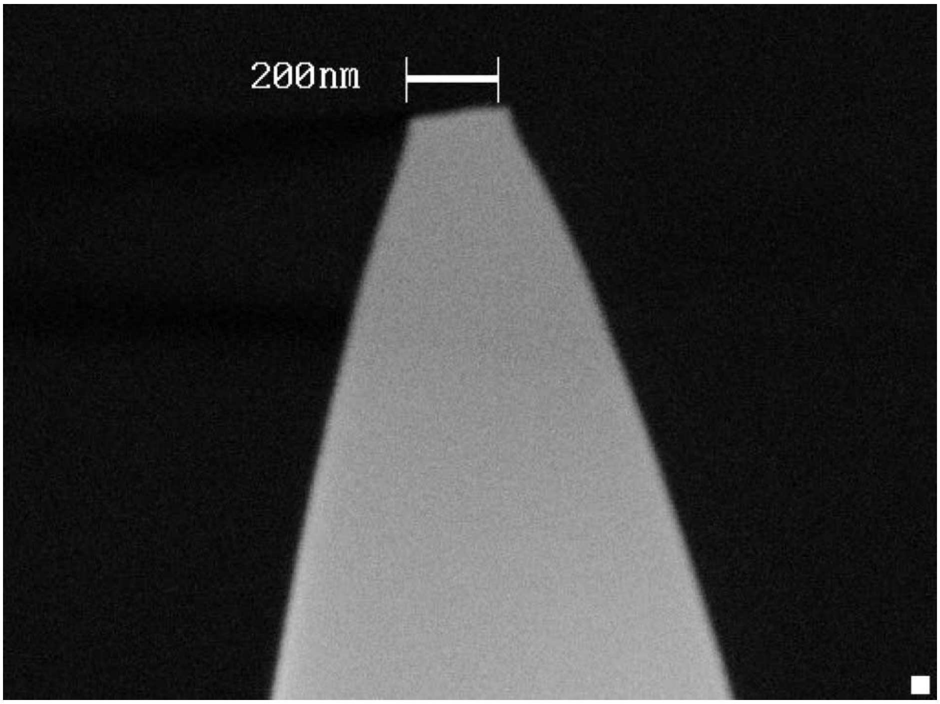

Fig. 2. An SEM image of a pulled optical fiber. The diameter of the pulled tip is 200 nm.

ion laser (488 nm) causes structural changes in the sample. The red light from the He–Ne laser (633 nm) which is outside the absorption band of both the *trans* and *cis* states of the azobenzene is used as the probe. The orientation of the polarization of the light from the He–Ne laser coming out of the tip is chosen such that the depolarization caused by the two right-angle prisms in the collection path is minimized. An interference filter is used to block both the blue light from the argon laser and red light from the feedback laser (670 nm) when probing the induced structural changes. A polarizer is used to analyze the polarization state of the probe beam. Before the sample is exposed to light from the argon ion laser, the polarizer is set to minimize the transmission of the light from the probe laser. In this way, we can measure the optically induced birefringence.

Initial experiments performed with a film of a side-chain liquid crystalline azobenzene polyester (see Ref. [9] for a description of the polyester) were not successful. We ascribe this to the aggregated domain structure in the film, which requires a melting and/or a reorientation of the domains for a detection of structural changes. The architecture of the polyester was then changed to make the main chain more rigid preventing the formation of liquid crystalline phases. As much as 4.2 mg of this polyester, denoted P6aA, was dissolved in 80 μl of chloroform and spin-coated on clean glass substrates. The thickness of the film was measured to be 380 nm by a Dektak 3010 profile measuring system. The sample was heated to 90°C for a few minutes and cooled rapidly down to room temperature before it was mounted in the near-field microscope.

For lithographic recording in the film, a line scan was performed in the middle of the scan range, typically set to 20 μm. As the scan rate is low (1 line/s), we could manually trigger the shutter for the argon ion laser and expose the sample during a part of a single line scan. When the shutter receives a trigger signal, it opens for a preset time (0.5 s) causing a 10 μm long line to be exposed. The power from the argon laser coupled into the fiber is 1 mW. About 1 nW is transmitted through the tip, corresponding to an intensity of 12 $\mathrm{W/cm^2}$. Multiple exposures can be made by scanning in a different direction.

Quite surprisingly, the scan with the probe beam revealed that only very little anisotropy was induced in the film, even though the intensity at the tip is larger than in the case of the far-field exposure (typically 300 $\mathrm{mW/cm^2}$). However, a detectable topographic feature with a typical surface height of approximately 6 nm was observed. An example of a scan with multiple exposure is shown in Fig. 3. A shear force image showing the change in surface topography is displayed. The two scan lines, each of about 240 nm in width are recorded in the polyester layer. The relatively large line width compared to the aperture diameter is attributed to the divergence of the beam before reaching the substrate through the thickness of the polyester layer (∼380 nm). Topographic features in polarization holographic gratings in azobenzene polyesters have been studied well before [10], as well as topographic features arising from a single-beam exposure [11]. However, it is quite surprising that topographic features should be more predominant than anisotropy when using near-field optical microscopy.

At the moment, the exact mechanisms for the presence of topographic features in azobenzene polymers are not clear. Many theories have been proposed so far, but none can explain the polarization dependence, as well as the nature of the different surface profiles [12–16]. Theories based on free volume changes and pressure gradients in the material due to the *trans–cis* isomerization and anisotropic diffusion do not explain the changes observed with different polarization. A gradient field theory [17] based on the sign of the susceptibility of azobenzene does not explain

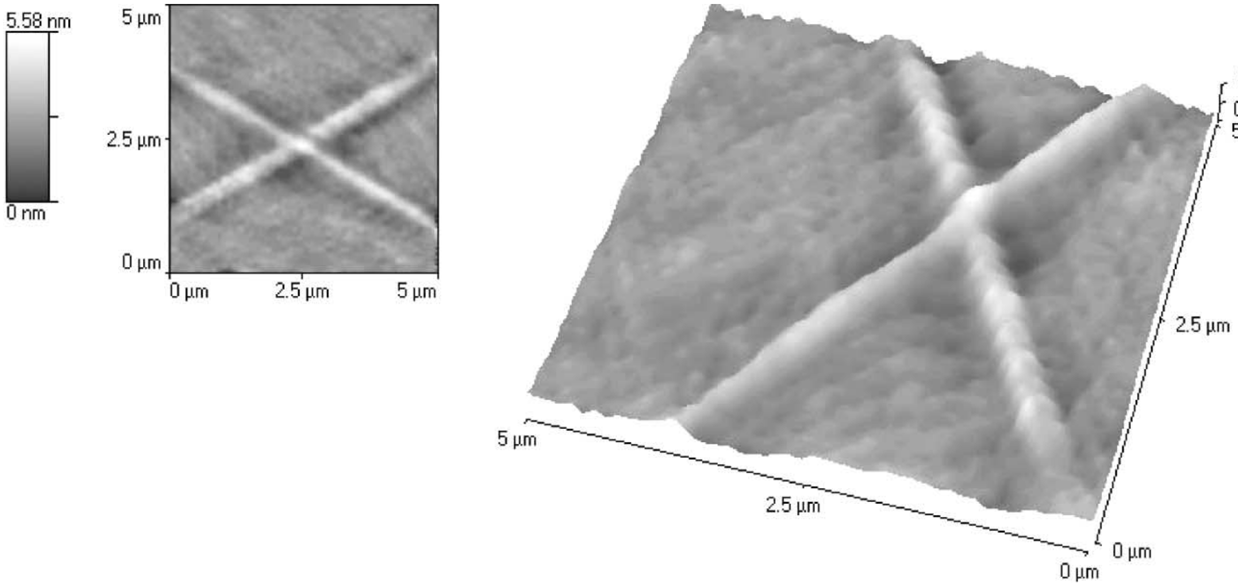

Fig. 3. Topographic image of the exposed sample. Typically an area of 5 μm × 5 μm is scanned. The maximum height in the figure is 5.7 nm.

peaks and valleys observed with the same chromophore, but different main chain structure. We believe that a mechanical deformation in the form of expansion or contraction is responsible for the surface relief. Using a floating drop experiment, we have shown that the drops either expand or contract depending on the polyester architecture [18]. We propose that an elastic deformation of the polymer due to the interaction between dipoles ordered through polarized light irradiation and the presence of a boundary layer as the possible cause for the surface relief [19].

Large topographic structures can also be observed when the azobenzene polymer films are irradiated with polarized light through a mask containing narrow features [20]. In the case of P6aA, for light polarized parallel to the grating vector, when the scan is performed at the edge of the Gaussian profile, topographic peaks have been obtained. Moving towards the center, i.e., increasing intensity, we find that the peaks evolve into trenches. We also observe this a time-dependent displacement between the topographic and anisotropic gratings in the case of polarization holography. Thus, the present observation of peaks in the surface relief is consistent with the transmission mask observations.

In conclusion, we have shown that it is possible to fabricate narrow topographical features in a thin film of a side-chain azobenzene polyester. This technique may be useful for high-density optical storage of information.

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