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Near-field optical writing on azo-polymethacrylate spin-coated films

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Abstract

We report on near-field optical writing and topographic reading of spin-coated azo-polymethacrylate films with subwavelength resolution. The sample is functionalized with photosensitive side chain azobenzene groups. These photochromes are locally illuminated at 325 and 488 nm through the aperture of a metalized tapered optical fiber. The printing on subwavelength scale is due to optically induced cooperative rearranging of the polymeric chain. It is read in situ in the surface topography imaged by shear-force microscopy. The stability of the optically produced pattern and the cycling characteristics of the photoisomerization of the azobenzene molecules make these samples suitable for optical nanolithography and high density optical data storage. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Near-field scanning optical microscopy; Optical data storage; Photosensitive side chain polymers

1. Introduction

Optical systems enable writing/reading without physical contact with the media, thus reducing wear and providing opportunities for the use of a number of different media. More significantly, they offer the prospect to store data at very high spatial density [1]. The scanning near-field optical microscope (SNOM) [2,3] is not diffraction limited. Thus, structures with transverse size well below wavelength can be produced for high density optical storage applications. A near-field optical resolution of $\lambda/10$, for example, provides a potential storage capacity of at least 1 Gbit/cm^2. Progress in optical storage has recently been made by using near-field optical techniques on polymer films. A SNOM combined with a photon scanning tunneling microscope (PSTM) has been used for spatially localized photobleaching on a spin coated polyvinypyrrolidone (PVP) thin film containing a new synthesized dye AF-380 [4]. One-photon writing and two-photon readback as well as two-photon writing and readout has been demonstrated using pulse excitation (80 fs with a repetition rate of 80 MHz) at 800 nm and frequency doubled at 400 nm. A bit diameter of 136 nm has been obtained, with the center-to-center distance

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of 258 nm, corresponding to 1.5 Gbit/cm^2. The storage induced by photobleaching is not, however, erasable and this dye-doped film can only function as a write-once read-many medium. Circular protrusions with a constant diameter of about 120 nm and height directly proportional to the irradiation time as well as an optical pattern with a resolution of about a tenth of the wavelength (55 nm) have been obtained with a homemade aperture SNOM on sol–gel films [5]. The samples were prepared from functionalized alkoxysilane monomers bearing bulky carbazole moiety (Si-K) and electron-donor/electron-acceptor substituted azobenzene (Si-DR1). The azobenzene moiety in this sample shows a broad absorption band between 400 and 600 nm. Near-field irradiation in this spectral region induces matter migration with subsequent film swelling locally under the SNOM tip. As in far field irradiation, this effect is likely generated by the azobenzene moiety movements induced by repeated *trans–cis–trans* isomerization cycles [6].

Here, we report on a similar writing/reading experiment performed with a SNOM on azo-polymethacrylate spin coated films. Spatial sub-wavelength resolution is demonstrated, proving the possibility of achieving re-writable high-density optical storage. For this azo-polymer, relaxation and dynamics studies have been recently reported on different length and time scales [7,8], as well as far field optical effects [8,9]. Homogeneity and optical response depend on side and main chain coupling, on mesogenic potential, on conformational main chain transitions [8,10], on glass transition and on *trans–cis* isomerization [11]. The relative weight of such physical processes, which is temperature dependent, can be altered also by optical pumping upon suitable irradiation [12]. At room temperature, u.v. or blue irradiation with energy density above a threshold of 0.06 J/cm^2 [9] and 1 J/cm^2 [13], respectively, markedly increases the *cis*-isomer fraction, resulting in frustration of the nematic phase.

Extensive studies on the dynamics of the different isomers and on the induction of anisotropy gratings at micrometer length scale in side chain azo-polymers are reported in the literature [14,15].

2. Experiment

The photosensitive material used in this work consists of a polymethacrylate (PMA) matrix, modified in the four position by the introduction of an azobenzene mesogenic unit (3-methyl-4′-pentyloxy) connected to the main chain by an hexamethylene spacer. The modified polymer (in the following denominated PMA4, for short), synthesized following a standard procedure [16], has a mean molecular weight 59.000 and a polydispersity 3.17. According to differential scanning calorimetry measurements [8], the material undergoes glass transition at $T_g = 294$ K. Above T_g, PMA4 has a nematic phase which persists up to the clearing temperature T_c observed at approximately 353 K. The spin coated films are prepared from a highly concentrated solution of PMA4 powder dissolved in chlorobenzene and stirred at room temperature for a few hours. Films of different thickness are easily prepared by depositing single drops of solution onto a Corning 4079 glass substrate and spinning at speeds ranging from 2000 rpm to 10 000 rpm. Their thickness, tested by means of an Alpha Step surface profilometer, ranges between 100 and 200 nm. The thinner film is chosen for the present experiment. Fig. 1 shows its absorption spectrum (bottom of the figure) together with the chemical structure of the PMA4 matrix (top of the figure). Before nanowriting, the PMA4 film was thermally processed following a procedure [8] that guarantees a macroscopically isotropic homogeneous substrate for optical nanorecording.

Our near-field optical microscope is based on a homemade setup [17], implemented with a tuning fork detection of the shear-force feedback [18,19]. For this experiment we use commercial (Nanonics) tapered optical probes with 100 nm nominal aperture. The optical fiber is coupled by a commercial coupler (OZ Optics HPUC style), either to a He–Cd laser at 325 nm to excite the π–π^* *trans–cis* isomer transition or to an Ar$^+$ laser at 488 nm to excite the n–π^* *cis–trans* isomer transition. The relative topographic efficiency of the two optical excitations are then easily deduced. The 488 nm laser light is, however, simultaneously responsible for the optical cycling of the *trans–cis–trans* isomerization, because the u.v. peaked *trans* isomer

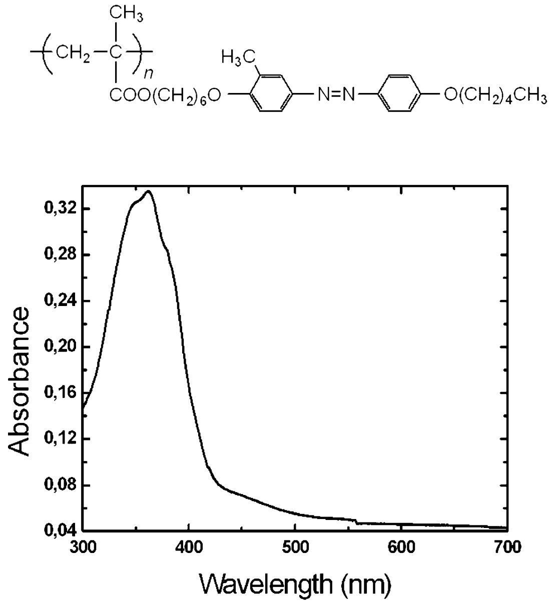

Fig. 1. Chemical structure of the polymer liquid crystal used in this study (top of the figure) and absorption spectrum (bottom of the figure) of the 100 nm thick PMA4 thin film.

absorption has a long tail in the blue. In far field, this cycle has induced birefringence in the azopolymer and hence provides an efficient writing mechanism, through the photoinduced side chain reorientation [8]. In the present near field experiment, for laser energy densities above threshold [9,13], photoinduced isomerization is accompanied by diffusion processes resulting in topological reliefs that are read in situ by the shear-force SNOM mechanism. A mechanical shutter equipped with a timer, is placed between the laser source and the laser-to-fiber coupler in order to inhibit the illumination of the sample after printing. The surface roughness of the sample is estimated, before of the experiment, by studying the topography image obtained with the SNOM shear force signal. The film is remarkably flat with an average roughness of a few nanometers.

3. Results and discussion

We believe PMA4 is a good candidate for rewritable information storage device because of its mesogenic character and its glass transition at room temperature. Liquid crystalline polymers with functional mesogenic side chain groups, exhibit mesomorphic properties of low molecular weight liquid crystals and the mechanical response of the polymeric materials [20]. In order to get quickly rearranged regions, in principle limited by slow diffusion processes, optical writing must be carried out above the glass transition temperature T_g of the polymer while data are stably stored either at temperatures below T_g or in the highly viscous liquid crystalline state. On the other hand, stability above the glass temperature T_g is, in the present case, assured by a main chain conformational transition that takes place at about 320 K [8]. Thus, liquid crystal polymers containing azobenzene dyes in the side chain are suitable for this application in which *trans–cis* isomerization can be induced photochemically in the aromatic azo group. *Trans–cis–trans* isomerization cycles, which take place at the nanosecond time-scale and at nanometer length-scale, are able to change the orientation of the azo dye molecules in the polymeric matrix with the resultant net effect of local realignment of the optical axis and modulation of the index of refraction at the illuminated spot [21]. Moreover, the photoinduced alignment can be enhanced by the possibility of cooperative behaviour driven by the self organizing properties of the liquid crystal polymer.

The optical absorption spectrum of Fig. 1 clearly indicates two main structures. The stronger one, located at about 360 nm, is attributable to the π–π^* *trans* isomer absorption that is responsible of the *trans–cis* isomerization of the azobenzene side group [22], linked to the main polymeric chain via a flexible spacer of the alkyl groups. A second weak absorption structure is centered at about 436 nm and attributable to a n–π^* excitation which leads to the *cis–trans* photoisomerization and to the tail of the π–π^* transition [23]. By near-field excitation in the u.v. as well as in the blue, we demonstrate the possibility of using the so-called optically induced cooperative rearranging of the polymeric chain [24,25] to store information on the material surface on a subwavelength dimension. The effect is demonstrated to work on both absorptions despite the different strengths of the two transitions.

The storage process was first obtained at room temperature, illuminating the surface with the HeCd laser line at 325 nm for 1 s, shuttering the laser beam and moving the optical tip driving the piezoelectric scanner of the SNOM along a user defined path. The laser power is about 2 mW at the laser-to-fiber coupler. The printing process was repeated until the drawing was completed. The image is inscribed in a 3.5 μm × 3.5 μm wide area and consists in an array of 21 single dots placed 500 nm one from the other to reproduce a geometrical shape. Fig. 2(a) shows the topographic image collected after the writing process. The sample surface topography is changed by the photoinduced processes and reproduces the path followed by the near field probe during the writing procedure. A line profile, (marked with a black line in Fig. 2(b) and analyzed along the *x* direction) reveals that the optical printing creates a number of well-separated embossed conical structures with a full width at half height of about 180 nm and a mean height of about 15 nm. The information was stable not only during the measurement time but also in the long term.

A similar topographic effect is observed by illuminating the sample surface with the Ar^+ laser line at 488 nm. In this case the laser power coupled to the SNOM fiber is 0.5 mW. The printing process was repeated three times, with 15, 30 and 45 s of exposure, to produce three dots placed along a line 500 nm one from the other. Fig. 3 shows the shear force image taken after this writing process and one topographic profile along the row marked with the a dashed line in the left of the picture. Despite the longer recording time, the dimensions of the dots are unchanged and the growth of the structure seems to be linear with respect to the illumination dose, at least in the investigated range. The longer recording time corresponds to a higher exposure time as required by the lower efficiency of the *trans* isomer illumination in the blue compared to the u.v. illumination.

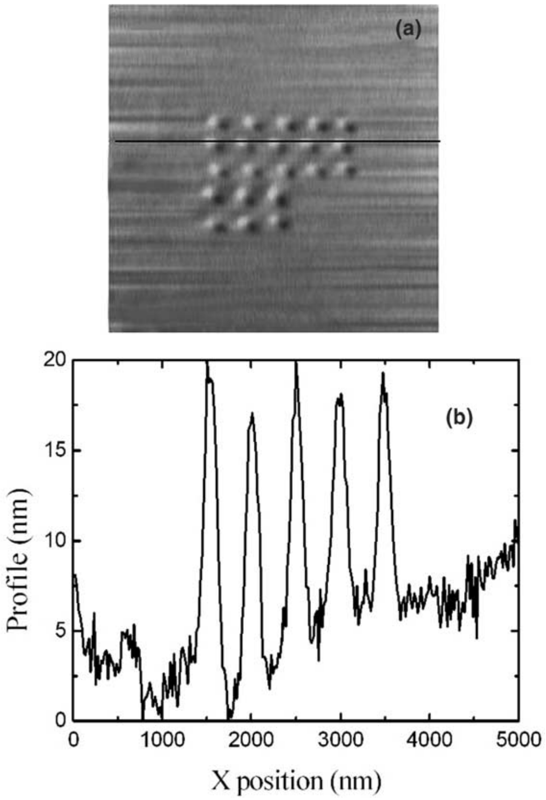

Fig. 2. (a) 5 μm × 5 μm shear force image of the pattern on the PMA4 film obtained illuminating the sample for 1 s at 325 nm. (b) Profile analysis along the black line marked in the image.

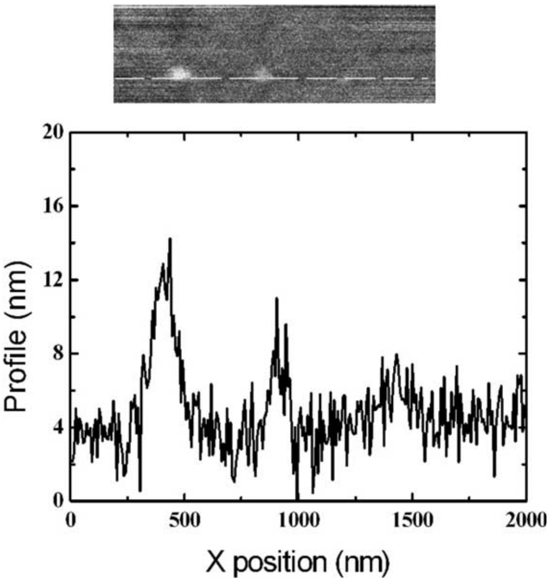

Fig. 3. Three dots obtained with different exposure times upon Ar^+ laser illumination at 488 nm. The embossing grows linearly with the exposure time.

The dimension of the structures may be affected not only by the size of the tip but also by the thickness of the film. Inside a thick film, at the depth where the near-field is overcome by the far-field, the subwavelength resolution is lost. Indeed, our observation on the 100 nm thick film is in agreement with the recent experiment of [5] where the 60 nm size was obtained only on the thin film of 20 nm. The long-term stability observed upon u.v. near-field irradiation is confirmed also in this case. In addition to the printing stability, we have found that the film can be easily erased by heating above the clearing point temperature for about 72 h. After thermal treatment the optical transmission results unchanged, the topography is again flat and the film surface is able to store new data with the same exposure time.

In conclusion we demonstrate the possibility of producing subwavelength topographic pattern on PMA4 thin film, either with u.v. and blue illumination, thus providing a potential application for high-density data storage. The material may be optically written and thermally erased at a relatively low temperature with no damage. Hence, it may be able to serve as rewritable high density media. Moreover, as the *trans–cis–trans* isomerization cycle of the chromophores is able to produce birefringence on the polymeric matrix [26], it may be usable in a rewritable high density storage device based on photoinduced birefringence by using near-field optical techniques. Work is in progress toward polarization control and analysis in near-field. Pure optical subwavelength writing/reading based on the birefringence properties of this material is indeed very appealing.

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