Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Sub-Micron Scale Optical Read/Write/Erase on Azo-Polymethacrylate Thin Films by Scanning Near-Field Optical Microscopy

Massimiliano Labardi [a], Nicola Coppedè [a], Lucio Pardi [a], Maria Allegrini [a], Marco Giordano [a], Salvatore Patanè [b], Antonella Arena [b] & Eugenio Cefalì [b]

[a] INFM and Dipartimento di Fisica "Enrico Fermi, Università di Pisa, Via F. Buonarroti 2, Pisa, I-56127, Italy

[b] INFM and Dipartimento di Fisica della Materia e Tecnologie Fisiche Avanzate, Università di Messina, Salita Sperone 31, Messina, I-98166, Italy

Version of record first published: 18 Oct 2010

To cite this article: Massimiliano Labardi, Nicola Coppedè, Lucio Pardi, Maria Allegrini, Marco Giordano, Salvatore Patanè, Antonella Arena & Eugenio Cefalì (2003): Sub-Micron Scale Optical Read/Write/Erase on Azo-Polymethacrylate Thin Films by Scanning Near-Field Optical Microscopy, Molecular Crystals and Liquid Crystals, 398:1, 33-43

To link to this article: http://dx.doi.org/10.1080/15421400390220962

Mol. Cryst. Liq. Cryst., Vol. 398, pp. 33–43, 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390220962

Taylor & Francis
Taylor & Francis Group

SUB-MICRON SCALE OPTICAL READ/WRITE/ERASE ON AZO-POLYMETHACRYLATE THIN FILMS BY SCANNING NEAR-FIELD OPTICAL MICROSCOPY

Massimiliano Labardi, Nicola Coppedè, Lucio Pardi, Maria Allegrini, and Marco Giordano
INFM and Dipartimento di Fisica "Enrico Fermi," Università di Pisa, Via F. Buonarroti 2, I-56127 Pisa (Italy)

Salvatore Patanè, Antonella Arena, and Eugenio Cefalì
INFM and Dipartimento di Fisica della Materia e Tecnologie Fisiche Avanzate, Università di Messina, Salita Sperone 31, I-98166 Messina (Italy)

Optical writing and subsequent optical reading of sub-micron size features has been obtained at room temperature on a spin-coated film of polymethecrylate added with azobenzene mesogenic side groups (PMA4), by means of scanning near-field optical microscopy (SNOM). Illumination with blue or UV light through the SNOM aperture induces conformational transitions in the side units, obtaining their orientation in a localized region. Optical writing and topographic reading with subwavelength resolution have been demonstrated. The pure optical readback is obtained by laser light at 690 nm through the aperture, in the polarization-modulation mode that provides sensitivity to dichroism and birefringence. Equally spaced lines have been written and subsequently imaged, presenting about one micron width in the birefringence image and about 600 nm width in the scattering optical image. Local erasure of optical information can be obtained by using green light at 543 nm with modulated polarization through the SNOM tip, in order to destroy the molecular alignment.

Keywords: SNOM; polarization contrast; azobenzene; polymeric liquid crystals; ultra-high density data storage

We thank M. Laus for providing the synthesized PMA4 polymer and G. Gorini for the loan of the He-Ne green laser source. We thank MURST for financial support through the project CIPE-Cluster 26.

INTRODUCTION

Recently, valuable progress has been made towards the achievement of optical ultra-high density data storage by applying the near-field technology to polymer films. An optical device for purely optical reversible write and read of sub-wavelength size bits is highly desirable, because of the potential enhanced speed and duration [1], combined to the increased density.

The near-field optical patterning of a photochromic sol-gel film, with the production of surface reliefs with lateral resolution of 55 nm, has recently been reported [2]. The sample contains the azobenzene moiety, which, under illumination, undergoes repeated photoisomerisation cycles associates to a matter migration. Light-induced mass transport is an interesting phenomenon, already investigated in various polymers [3]. However, the actual mechanisms of mass-transport induced in the near-field with their connected surface modifications are not yet fully understood in materials containing the azobenzene moiety. Experiments so far, have proved that both topographic effects (embossing) as well as optical effects (dichroism and birefringence) can be produced. These results make azobenzenes good candidates to produce optically re-writable high density data storage supports, on condition that a suitable write/read/erase method is provided.

Recently, we have reported near-field optical writing and topographic reading of spin-coated azo-polymethalcrylate film with subwavelength resolution [4]. Here, we report on write/read/erase experiments by using a SNOM modified to detect the local optical anisotropy (dichroism or birefringence) of the sample. Sub-micron optical modification of the sample is demonstrated as well as the embossing of the surface on a sub wavelength scale. The dependence on temperature and optical power of the write speed is also studied. Finally, the optical erasure process is investigated in order to demonstrate the potentiality of the material as a high density optical re-writable medium.

EXPERIMENT

Setup

The experiments have been conducted by means of a home-made SNOM implemented with polarization modulation, similar to the ones described in Refs. [5] and [6] but preparing the laser light at 690 nm with rotating linear polarization at 125 Hz (Fig. 1).

The optical signal is collected in transmission mode by a 0.5 N.A. aspheric lens and detected, through a linear polarizer, by a photomultiplier tube; an interferential filter tuned at 690 nm is placed in the optical path to improve the signal/background ratio. The modulated signals are detected in

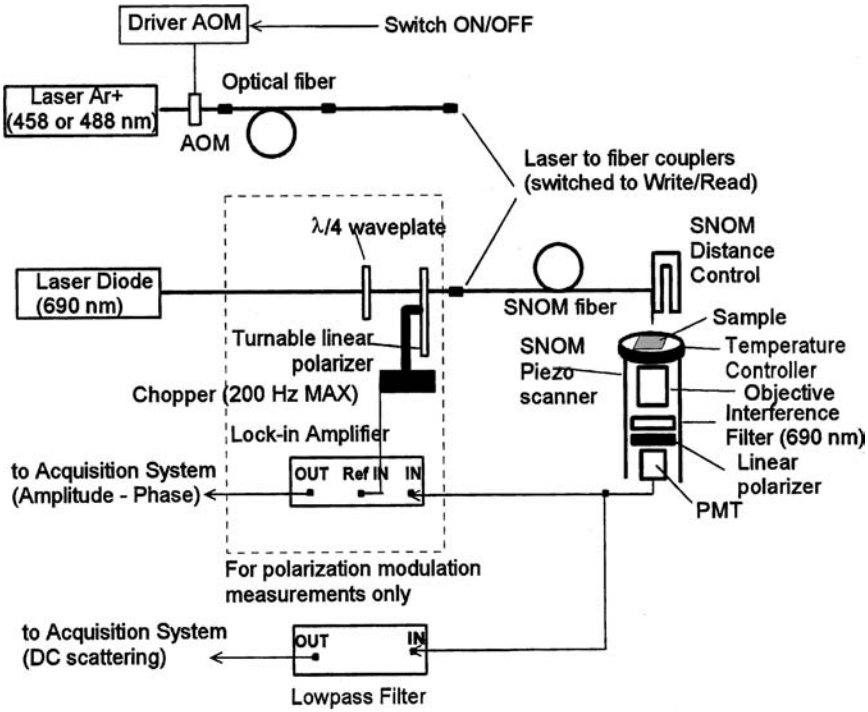

FIGURE 1 Experimental setup for polarization-modulation SNOM and optical writing experiments.

amplitude and phase by a lock-in amplifier, typically operated with 100 ms integration time. The DC SNOM scattering signal is extracted by filtering out the higher frequencies with a 10 Hz cut-off low-pass filter.

The distance between the optical probe and the sample is stabilized with a shear force feedback based on the well-known tuning fork method [7]. Such a system is suitable for optical nano-reading experiments since it avoids the stray light present in the optical detection systems. The probe is laterally oscillated at the tuning fork resonance frequency (around 32.7 kHz) with typical amplitude of 3 to 5 nm peak to peak; the estimated tip/sample working distance is of the same order of magnitude.

The SNOM sample holder is equipped with a home-made temperature controller [8] for in-situ annealing and temperature stabilization of the sample in the range −30 to +90°C.

The writing at 458 and 488 nm is obtained using an Ar^+ laser switched on and off by means of an acousto-optical modulator (AOM); the shorter UV wavelength at 325 nm is provided by a HeCd laser. Both the light

sources work at a fixed polarization. For the experiments of optical erasure, a green He-Ne laser at 543 nm, with rotating linear polarization, has been employed.

We use commercial SNOM sensors [9] consisting of an *Al*-coated tapered optical fiber, either single mode at 1.5 microns, or multimode UV for the experiments with the HeCd source. The instrument is equipped with a simple CAD software module able to drive the scanner along a defined path with speeds ranging from a few nm/sec to some microns/sec.

Samples

The photosensitive material consists of a polymethacrylate (PMA) chain, modified in the fourth position by the introduction of an azobenzene mesogenic unit (3-methyl-4′-pentyloxy) connected to the chain by an hexamethylene spacer (PMA4). 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 optical absorption spectrum of the material has two main features: a strong peak located at 360 nm and a second weaker structure at 436 nm. The first one is attributable to the π–π^* trans isomer absorption and is responsible of the trans to cis isomerization of the azobenzene side group linked to the main polymeric chain [10]. The second weak absorption structure is partially superimposed to the tail of the first one and is due to a n–π^* excitation which leads to the cis-trans photoisomerization [11]. Photon absorption may lead to a complete trans-cis-trans isomerization cycle, which makes the molecule to move in the direction of the light polarization and causes deformation of the polymeric network [12,13].

The samples for nanorecording are prepared from a highly concentrated solution of PMA4 powder dissolved in chlorobenzene; the solutions are stirred for a few hours at room temperature to avoid inhomogeneity. Ultra thin films, suitable for the optical nanowriting, are obtained by depositing single drops of solution onto a Corning 4079 glass substrate and spinning at speeds ranging from 2000 rpm to 10000 rpm. The thickness of each sample, tested by means of an Alpha Step profilometer, ranges from 100 to 200 nm depending on the spinner speed. Finally, to guarantee the homogeneity of the films, the samples are thermally processed for 24 hours at 343 K, resulting in a remarkably flat surface with an average roughness of a few nanometers, suitable for optical and topographic nanorecording.

TOPOGRAPHY READ/WRITE

The storage process is first obtained at 291 K illuminating the surface, through the near field probe, with the 488 nm Ar^+ laser line for 40 sec with

a power of about 20 nW estimated by the nominal throughput of the fiber. The laser beam is shuttered after every dot print and the sample is moved under the fiber tip by driving the piezoelectric scanner of the SNOM along a user defined path to write the shape of the alphabetic character *I*. Figure 2 shows the shear force image acquired immediately after the printing process. The wider dot printed in the right top part of the picture is due to a longer exposure time in which we aligned the laser to fiber coupler.

A line profile along the x direction (Fig. 3) reveals that the optical printing creates a number of well-separated embossed conical structures with a full width at half maximum (FWHM) of about 85 nm and a mean height of about 15 nm. The information appears to be stable not only during the measurement time but also in the long term.

A more complex, continuous line draw, showed in Figure 4a, is printed by exposing a film to the unshuttered 325 nm laser light. The optical probe is driven along the sample surface, following a pre-defined path, at a speed $v = 22$ nm/sec. During the writing process the sample temperature is fixed at about 297 K and the power I at the end of the optical probe is estimated to be about 5 nW, providing a fluence $F = I/(v\ a)$ of about 200 J/cm^2 assuming a tip diameter of 100 nm.

The shorter wavelength allows a higher writing speed thanks to the high UV excitation rate of the π–π^* trans isomer transition. The higher temperature also supports the write speed because the material is closer to the glass transition temperature, thus the molecules under illumination suffer lower hindrance to their light induced displacement, which is the ultimate responsible of the surface embossing. The line profile analysis (Fig. 4b) highlights that the structures have a FWHM of about 75 nm and a mean height of about 10 nm.

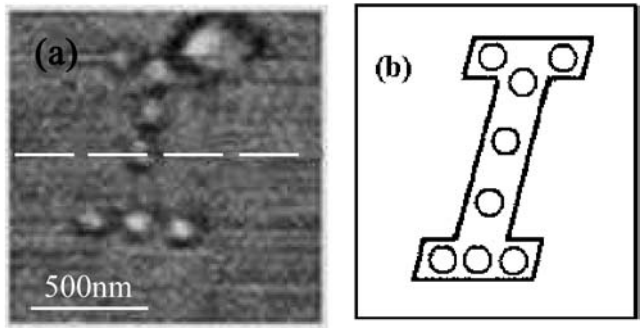

FIGURE 2 (a) Shear force image of the PMA4 thin film acquired after the printing process with $\lambda = 488$ nm, and (b) the schematic position of the dots written to reproduce the alphabetic character "*I*".

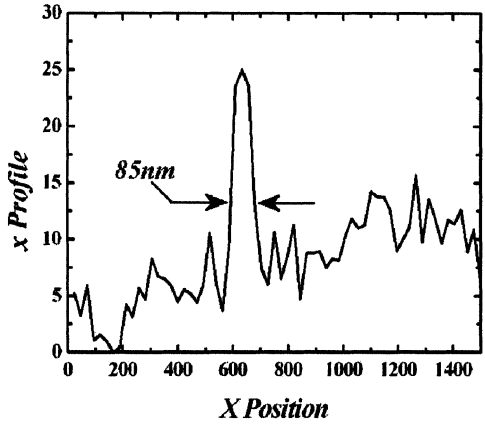

FIGURE 3 Profile analysis carried out along the white line marked in the shear force image of Figure 2.

The write speed clearly depends both on the wavelength and temperature but also the fluence plays an important role. The fluence is limited by the optical fiber aperture that, in turn, determines the lateral dimension of the structures. Figure 5a shows the shear force image of a nanostructured PMA4 thin film obtained at 301 K and illuminating the sample surface with the 325 nm laser light using an optical probe about 200 nm wide. The greater diameter a produces a fluence of about 1000 J/cm^2 able, in these conditions, to write the material at a speed $v = 250$ nm/sec. The line profile

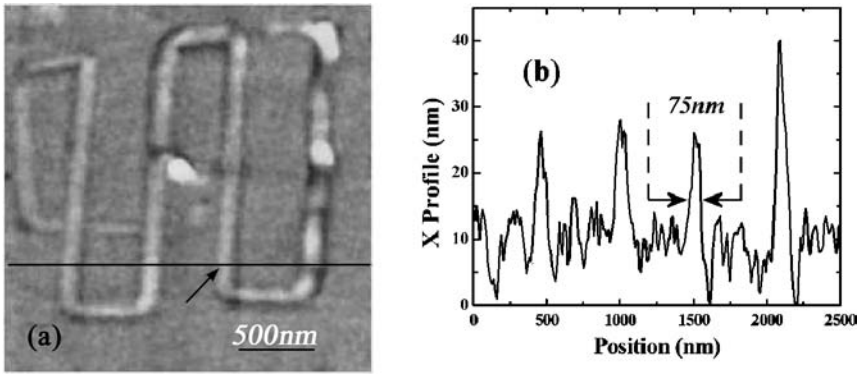

FIGURE 4 (a) Shear force image of the optically nanostructured PMA4 surface ($\lambda = 325$ nm, $T = 297$ K, $v = 22$ nm/sec) and (b) line profile extracted along the line marked in (a).

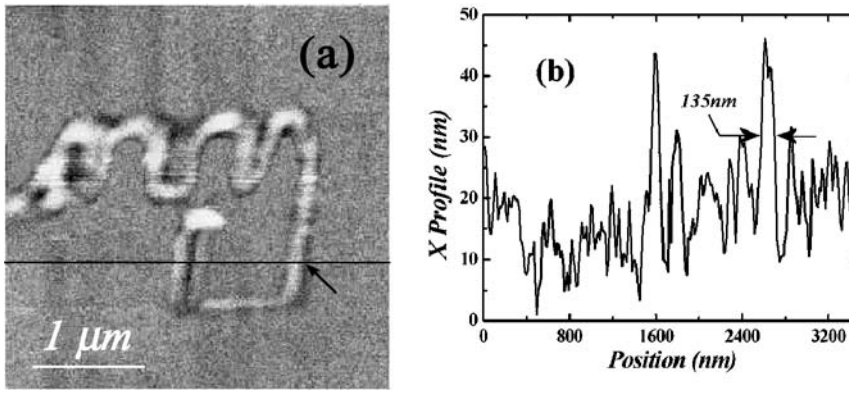

FIGURE 5 (a) Shear force image of the optically nanostructured PMA4 surface ($\lambda = 325$ nm, $T = 301$ K, $v = 250$ nm/sec) and (b) line profile extracted along the line marked in (a).

(Fig. 5b) reveals that the structures have a FWHM of about 135 nm, since the wider aperture produces a loss in the lateral resolution because of the larger illuminated area.

OPTICAL READ/WRITE/ERASE

Polarization-modulation Contrast

Polarization modulation SNOM is based on the different optical response of materials to different polarizations of light generated at the aperture. In the case of large apertures ($\sim \lambda/2$) the emitted light has mainly far-field character and is strongly diffracted after the aperture; nevertheless, its polarization lies basically on the sample plane, orthogonal to the tip axis. If the sample presents non-uniform and anisotropic optical properties, it may exhibit local changes of the (average) refractive index, as well as birefringence, dichroism, and topographic features able to influence the light scattering at different polarizations for geometrical reasons. These will show up differently in the demodulated optical amplitude and phase images.

Sensitivity to different optical properties can be obtained by using different kinds of analyzers in front of the detector (Fig. 1), like linear or circular polarizers, or by removing the filters. Birefringence causes the polarization direction of light to be varied with no intensity change, thus polarizers are needed to evidence the effect of modulation. On the contrary, dichroism provides anisotropic change in absorption of light, and thus it is evidenced by removing any polarizer from the detector path.

Spontaneous Optical Domain Arrangement

The optical appearence as revealed by SNOM of a PMA4 thin film after thermal annealing at 358 K for 24 h and subsequent fast cooling to room temperature (300 K) is shown in Figure 6. Reading has been accomplished by polarization modulation SNOM with 690 nm laser light (estimated output power $I = 500$ nW, tip diameter $a \approx 250$ nm). Randomly distributed optical features of micrometer size are present in both polarization modulation amplitude and phase images. The spontaneous optical domains look stable at least within few hours, as demonstrated by repeated scans.

Optical Features Writing

Optical lines inscribed in the PMA4 film are shown in Figure 7. The lines have been impressed by moving the SNOM tip at the constant speed of $v = 30$ nm/s while 458 nm laser light was coupled to the SNOM fiber (estimated output power $I = 50$ nW, tip diameter $a \approx 250$ nm, estimated tip/sample distance $d = 5$ nm). The resulting fluence is 670 J/cm^2. Such fluence value is enough to produce discontinuous topographic reliefs, while the corresponding optical signal is uniform along the lines.

The interlaced writing of adjacent lines in opposite directions (top to bottom and bottom to top) has produced a substantially difference result. Lines traced from top to bottom have resulted much more pronounced than the ones traced from bottom to top. This is ascribed to the well-known effect of a different working distance of the SNOM tip while scanning in opposite directions over an inclined plane. This suggests a strong effect of the tip/sample distance on the writing efficiency.

The lines in the amplitude image show a FWHM of 600 nm. The same lines in the phase image present a FWHM of 1 μm. Reliefs in the topography

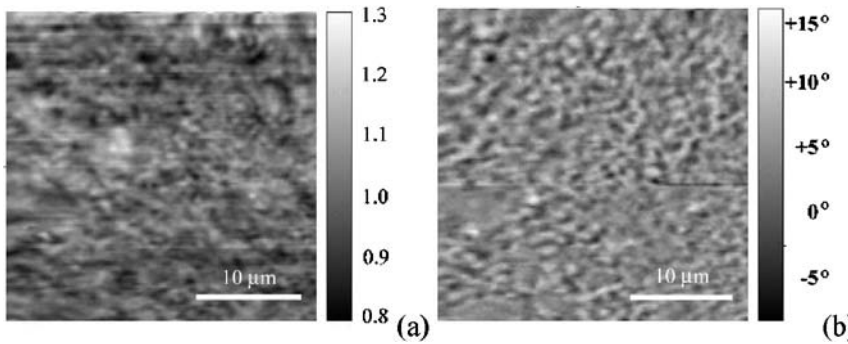

FIGURE 6 Polarization modulation SNOM amplitude (a) in arbitrary units, and phase (b) of spontaneous optical domains in the PMA4 thin film.

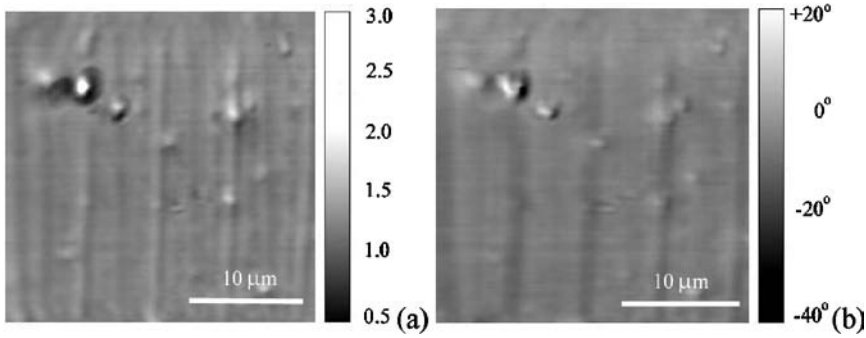

FIGURE 7 Polarization modulation SNOM amplitude (a) in arbitrary units, and phase (b) of written optical lines in the PMA4 spin-coated thin film.

exhibit smaller width (400 nm) and are mostly uncorrelated with the optical features. The different appearance and width of the lines provides evidence of the different character of the images. In particular, the optical orientation seems to spread over a wider region, while the orientation degree (order parameter) is more pronounced in the center of the lines. Furthermore, mass migration, if any, seems to take place within an even more limited region. Similar writing with 488 nm laser light and 500 nW output power from the SNOM tip has shown fragmented as well as continuous topographic lines, indicating that the used combination of fluence and wavelength were close to some threshold for the writing of topographic reliefs. The imprinted optical information has shown to be stable at room temperature for at least one day. Annealing treatment as well as ageing, have a pronounced effect on the storage ability of the films that loose efficiency with time and become hardly writable with the same parameters used previously. The storage performances can be partially restored by repeated annealing.

Erasure of Optical Features

A sequence of optical images after writing three vertical lines with 458 nm light is reported in Figure 8. The topographic image (Fig. 8(a)) shows discontinuous topographic reliefs in correspondence with the tracked lines. In the optical (DC) images, dark lines appear also in the regions where topographic reliefs are absent (for instance, the upper part of the line on the left). Images from (b) to (f) have been acquired at 20 min. intervals, by using as the readback unit a green He-Ne laser at 543 nm prepared with the polarization modulation. The used wavelength is close to the tail of the absorption band due to the conformational transitions of PMA4, thus slight

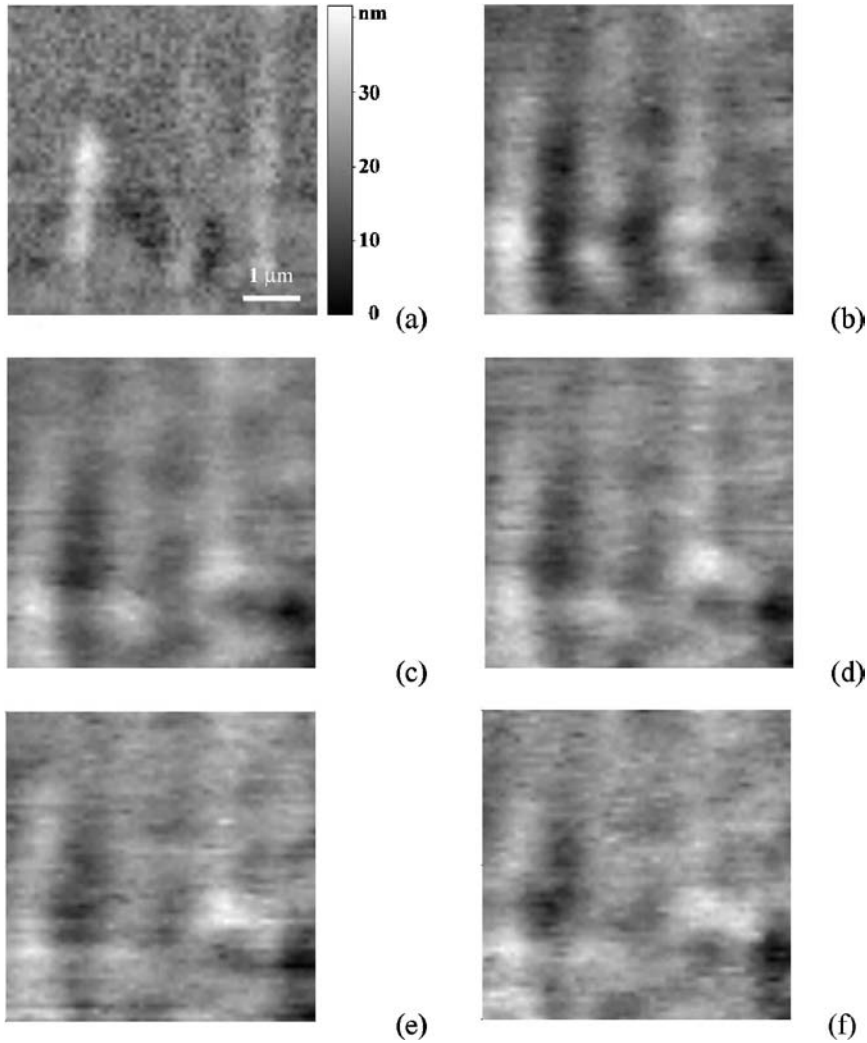

FIGURE 8 Topography (a) and sequence of DC SNOM optical images (b–f) taken at intervals of 20 min, showing the disappearing of optical signal due to the action of polarization-modulated green light. The average contrast of the optical images decreases as (b) 24%, (c) 18%, (d) 16%, (e) 14%, and (f) 9%.

absorption occurs also at this wavelength. Since the provided polarization is not fixed, though, the effect is to induce disorder in the orientation of the previously ordered chromophores, and then to erase the optical lines, as it is evidenced by the images sequence. The optical orientation persists

where topographic reliefs are present, indicating that the main chain rearrangement influences the average optical orientation of the chromophores so that it is more difficult to erase such areas. This experiment demonstrates the possibility of local all-optical reversible writing/reading and erasure of optical information.

CONCLUSION

Demonstration of sub-micron optical modification of PMA4 thin films deposited by spin coating has been given by means of polarization- modulation SNOM. Reversible writing has been also assessed on the same length scale. The topographic writing studies, performed both by using UV light and by increasing temperature, evidence that subwavelength features can be written as topographic reliefs and that they are accompanied by orientation of the chromophores. According to the experimental result, it seems that, with a further improvement in the sensitivity, our technique could provide an efficient high-density optical storage/read-out facility. Future work is thus aimed to the enhancement of signal-to-noise ratio for detection of small SNOM optical signals in the polarization-modulation mode.

REFERENCES

[1] (2001). In: *Fifth International Symposium on Optical Storage, Proceedings*, Gan, F. & Hou, L. (Eds.), SPIE, Vol. 4085.
[2] Landraud, N., Peretti, J., Chaput, F., Lampel, G., Boilot, J.-P., Lahlil, K., & Safarov, V. I. (2001). *Appl. Phys. Lett.*, *79*, 4562.
[3] Wuestneck, R., Stumpe, J., Karageorgieva, V., Meier, L. G., Rutloh, M., & Preshler, D. (2002). *Colloids and Surfaces: Physicochemical and Engineering Aspects*, *198–200*, 753.
[4] Patanè, S., Arena, A., Allegrini, M., Andreozzi, L., Faetti, M., & Giordano, M. (2002). *Opt. Commun.*, *210*, 37.
[5] Camorani, P., Labardi, M., & Allegrini, M. (2001). *Mol. Cryst. Liq. Cryst.*, *372*, 365.
[6] Ramoino, L., Labardi, M., Maghelli, N., Pardi, L., Allegrini, M., & Patanè, S. (2002). *Rev. Sci. Instrum.*, *73*, 2051.
[7] Karrai, K. & Grober, R. D. (1995). *Appl. Phys. Lett.*, *66*, 1842.
[8] Italian Patent GE2000A0000101.
[9] Nanonics Supertips Inc., Jerusalem (Israel), Model FN-50.
[10] Hviilsted, S., Andruzzi, F., Kulima, C., Siesler, H. W., & Ramannujam, P. S. (1995). *Macromolecules*, *28*, 2172.
[11] Ichimura, K. & Morino, S. (1998). *Appl. Phys. Lett.*, *73*, 921.
[12] Adam, G. & Gibbs, J. H. (1965). *J. Chem. Phys.*, *43*, 139.
[13] Cristofolini, L., Arisi, S., & Fontana, M. P. (2000). *Phys. Rev. Lett.*, *85*, 4912.