Reversible Purely Optical Nanowriting

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There is a great deal of interest in using nanophotonics tools in order to induce controlled modifications of materials and surfaces at the nanometer scale. In particular, photoactive materials, i.e., smart systems whose optical properties can be modified upon optical stimulation, can be efficiently used to achieve optical nanowriting.

Block copolymers were prepared from azobenzene methacrylate (MA4) and methyl methacrylate (MMA). The former monomer was introduced as both a photoresponsive and a mesogenic component, and the latter as a transparent non-mesogenic component. Thin films (100-500 nm thick) were prepared on glass through spin-coating. Due to repeated trans-cis and vice-versa photoisomerization cycles joined with strongly anisotropic absorption coefficient, exposure to linearly polarized light at 473 nm leads to modify the material birefringence. In macroscopic experiments, stable modifications could be induced also by using relatively short and weak laser pulses (0.1 ms and 1 μJ energy) [1].

Nanowriting on such films was accomplished by using a custom-made scanning near-field optical microscope equipped with polarization modulation (PM-SNOM). The setup was based on an aperture probe consisting of a tapered and metalized optical fiber. Being the transfer of polarization into the near-field a crucial issue for the success of the experiment, selected probes were used owning negligible spontaneous birefringence in the operating conditions of the investigation. The microscope was used in the emission-mode configuration, the interaction with the near-field being measured in transmission, i.e., by using a miniaturized photomultiplier mounted below the semi-transparent sample.

Writing and readout were realized in two subsequent steps, where linearly polarized radiation at 473 nm and polarization modulated radiation at 690 nm (a wavelength not absorbed by the material) were employed, respectively. The polarization-modulation setup was based on a photoelastic modulator configured in order to launch into the near-field probe light with a polarization state modulated at 50 kHz. Demodulation of the signal detected by the miniaturized photomultiplier at such a frequency enabled sensitivity to the material birefringence.

Typically, experiments consisted of a writing step achieved by scanning along a single vertical line the film upon linearly polarized absorbed radiation. Subsequently, the written area was imaged upon polarization-modulated conditions in order to build material birefringence maps. A topography map was simultaneously produced through the shear-force method. Results [2] demonstrated the ability to nanowrite the material, i.e., to produce localized stable modifications of the birefringence. In all the explored range of parameters, negligible topographical changes were observed. This finding, which is in contrast with previously reported experiments, is due to the low energy density delivered onto the material as a consequence of a relatively fast exposure (typical writing speed 1-2 μm/s), and to the properties of the block copolymer matrix, which favors the rearrangement of the azobenzene photoisomerized moieties. Remarkably, the absence of morphological modifications made possible an almost complete recovery of the original material optical properties upon exposure of the written surface to light polarized along a 90 degree rotated direction, as shown in Figure 1.

Exploration of the maximum spatial resolution attainable in the experiment was carried out by holding the near-field probe at preselected positions and shining the material with linearly polarized radiation. Isolated features showing a fwhm transverse size on the order of 50-70 nm were

produced in the birefringence maps. The achievement of smaller feature size was hampered by two factors due to the aperture size of the near-field probes, 50 nm nominal, and to the occurrence of spontaneous birefringence domains in the materials associated with the phase segregation of the copolymer blocks.

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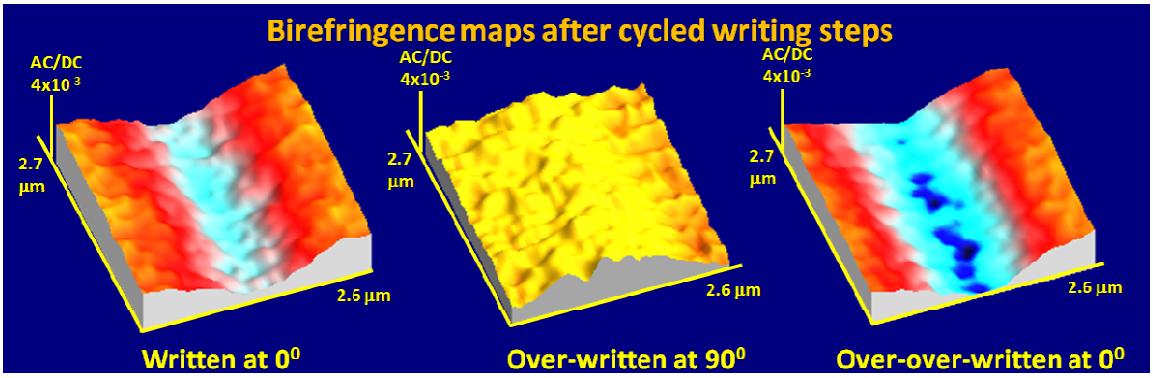

Figure 1. Birefringence maps of the same area of the film acquired upon exposure at linearly polarized radiation oriented at 0 degrees, first overexposure at the right angle, second overexposure at the original angle (writing speed 1.25 µm/s in all cases).

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2. F. Tantussi, S. Menghetti, E. Caldi, F. Fuso, M. Allegrini, G. Galli, *Appl. Phys. Lett.* **100**, 083103 (2012).

Francesco Tantussi received the Master Degree in Physics in 2002 and the PhD in Applied Physics in 2006 from Università di Pisa. He was then the recipient of different post-doc grants from Università di Pisa and INFM-CNR, and starting from 2009 he was a Researcher of the Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia, CNISM. His research interests cover a broad range of topics in structure of the matter, materials science, nanotechnology. During his PhD, he was involved in a European research project aimed at using laser cooling and manipulation of neutral atoms for nanotechnological purposes. Later on, he moved on the development and application of advanced scanning probe microscopy techniques. Within the NanoLab led by Prof. Maria Allegrini, he worked on a variety of near-field techniques, for both sub-micrometer investigation of materials and nanostructures, and for nanofabrication through optical nanowriting. Within this context, he applied polarization-modulation techniques for the analysis at the nanoscale of optically-active systems, including organics, carbon nanotubes, plasmonic waveguides and concentrators. He is the coauthor of more than 20 refereed papers in international journals and conference proceedings.