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Photochromic Sol-Gel Films Containing Dithienylethene and Azobenzene Derivatives: From the Design of Optical Components to the Optical Data Storage

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This work is devoted to photoresponsive hybrid organic-inorganic materials prepared by the sol-gel method, using dithienylethene or azobenzene as photosensitive chromophores. These photochromic units were covalently attached to the silica backbone as part of the main-chain and as a side group respectively. The electrocyclization of dithienylethene or the isomerization of azobenzene under irradiation cause local modifications of the optical properties of the host sol-gel polymers We took advantage of either high refractive index changes ($>10^{-2}$) or material deformation of the sol-gel films to design optical components and to store information.

Keywords: Dithienylethene; Azobenzene; hybrid material; sol-gel; data storage; optical components

I. INTRODUCTION

The sol-gel process is established as a convenient synthetic procedure to trap organic molecules in silica-based matrices [1]. The chemistry involved in this process is based on hydroxylation and condensation of molecular precursors in solution at room temperature. Physical properties of the resulting materials are determined by (a) the nature of the alkoxide type precursors and of the doping molecules, (b) the synthesis parameters and, (c) the condensation degree of the oxide network. Thus hybrid organic-inorganic materials exhibiting both

good optical qualities and mechanical strength were prepared with a variety of shapes (including thin films and monoliths) to serve as optical components [2]. A number of xerogel materials whose optical properties are governed by the interactions between the optically active system and the matrix have been previously reported [3]. Herein we investigate sol-gel films incorporating individually dithienylethene derivative and photochromic azobenzene. The active systems (photochromes) are covalently attached to the silica backbone through a flexible spacer. This approach results in a very high content of photochromes in matrices. Our interest in these materials stems from their potential application to the design of optical components and to optical data storage.

II. PHOTORESPONSE OF HYBRID THIN FILMS CONTAINING DITHIENYLETHENE DERIVATIVES.

Dithienylethenes, representative organic photochromic compounds, are receiving much current attention because of their potential application in devices exhibiting photoswitched properties [4]. Their photoinduced electrocyclization is responsible for the increase in the electronic delocalization of the molecule, generating an increase of the polarizability of the photochrome electronic cloud and a large change in the UV-visible absorption spectra. This results in the change of the refractive index of the medium in which they are incorporated. Our recent investigations in this field revealed that this effect was increased as the photochrome content increased [5]. This effect is illustrated in figure 1.

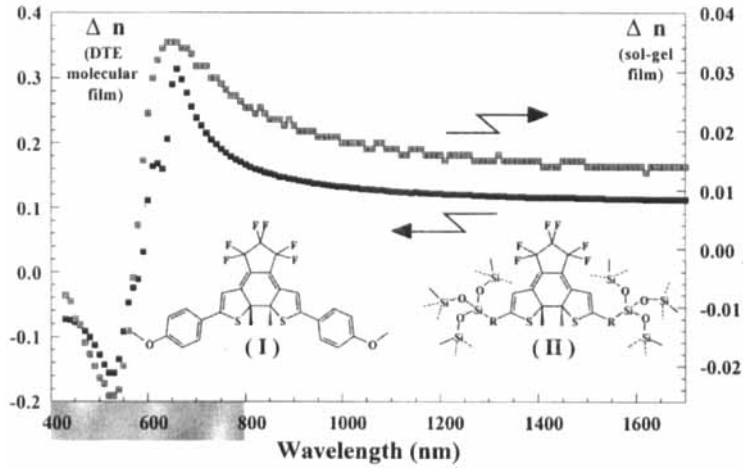


FIGURE 1 Refractive index changes as a function of the wavelength (the grey area demarcates the spectral region of the visible absorption peak).

Through ellipsometry measurements performed on a pure dithienylethene **(I)** film, we show that the refractive index change Δn can reach high values, even in the non-absorbing region of the molecule (i.e. 0.12 at 1300nm). However, the sample prepared from dithienylethene tetrahydrofuran solution spin coated on a glass substrate remains mechanically brittle. The same experiment performed on hybrid materials in which the photochromic groups **(II)** belong to the polymer network resulted in high changes of refractive index even if the photochrome content is lower (i.e. 0.015 at 1300nm). Photochromic properties of the sol-gel films were used for writing channel waveguides, gratings and others patterns utilized in integrated optics. The photochrome-containing xerogel films, previously discolored by an expanded argon laser beam at 514 nm, were colored through a mask by UV irradiation (312nm) to generate complex high-refractive index waveguide patterns [5].

As previously mentioned, the photoinduced electrocyclization of the molecule produces both an important modification of the absorption spectrum and a change of the refractive index in the transparency region of the material. Additional informations on the system include : (a) the optical properties of the individual molecule are strongly anisotropic, (b) the orientation of the photochromic units is fixed thanks to their specific functionalization (covalent grafting to the silica backbone) and, (c) the photochemical transition of dithienylethene molecules is not thermally reversible. Therefore, the discoloration with a linearly polarized light can induce a macroscopic optical anisotropy in the material which results in a linear dichroism in the visible absorption band and in an important birefringence $\delta n(t)$ in the near-infrared transparency region [6]. The principle of the experiment and results are depicted in figure 2a and 2b respectively.

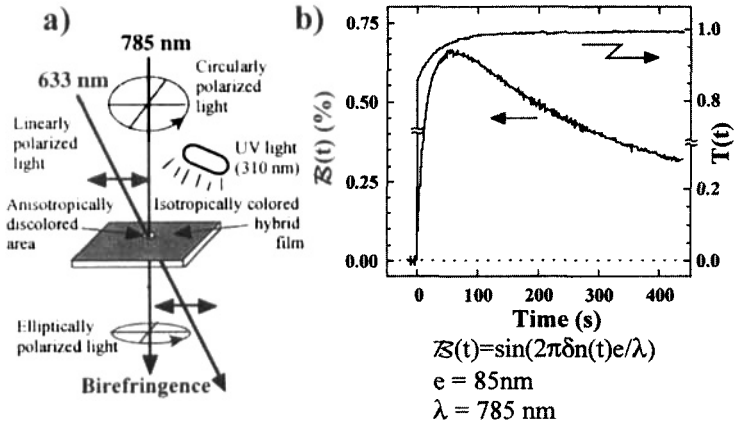


FIGURE 2 a) Experimental set-up; b) Time recording of the birefringence signal $\mathcal{B}(t)$ at 785 nm and the optical transmission of the film under illumination with a linearly polarized light (633 nm).

As shown there, at a characteristic exposure time τ, the birefringence reaches a maximum value and then decreases slowly. When the discoloring light is turned off, the birefringence remains constant. In terms of application to data storage, the values of τ and of $\delta n(\tau)$ determine the maximum speeds for the writing and the reading process respectively. In the experiment presented here, τ was of about 50 s for the incident power density of 0.25 $nW.\mu m^{-2}$. In order to achieve a writing speed of 1 MHz, an incident power density of 12.5 $mW.\mu m^{-2}$ is needed. It is worth noting that only 15% of the incident power is actually absorbed in the film. However, the writing energy can be substantially reduced through discoloration using a shorter wavelength near the maximum of the visible absorption band (typically 580 nm) for which the absorption coefficient and particularly the photochemical quantum yield (as small as 0.43×10^{-2} in the present experiment) are larger. For the reading process, let us first emphasize that it is non-destructive since the reading wavelength is out of the absorption bands, then note that the value of $\delta n(\tau) = 0.01$ is already largely compatible with the reading speed of commercial systems like magneto-optical devices.

III. PHOTORESPONSE OF HYBRID THIN FILMS CONTAINING AZOBENZENE DERIVATIVES.

Azobenzene and its derivatives can also be used as photochrome units in optical storage materials [7]. Azo dyes, when irradiated by visible light, undergo trans-cis isomerization. Following a photochemical or thermal path, the cis form reverts slowly (at room temperature) to the thermodynamically more stable trans isomer. The photoisomerization can be much more rapid at room temperature if an electron-donor substituent is present in the para position of one of the phenyl rings and an electron-acceptor substituent is present in the para position of the other ring. During the course of isomerization, azobenzene undergoes a large structural change which affects the medium arround the molecules [8]. Recently a new application for azobenzene functionalized polymers has been proposed in the form of laser-induced surface relief gratings [9]. We now report the procedure for inscribing stable surface relief gratings having high modulation depth on hybrid films.

First, silica-based materials containing azo and large carbazole side groups were prepared from modified silane monomers copolymerized with tetraethoxysilane [10]. To record significant film deformation, the silica network has to be weakly cross-linked. The surface gratings were written with an interference pattern created from coherent Ar^+ laser light at a wavelength (514nm) located inside the absorption band of the material. The laser beam was divided into two polarized beams of equal intensity, which interfere onto the sample. The angle between the two beams determines the grating period. The energy density of the incident writing beams was low enough to avoid photobleaching. The evolution of the optically induced grating was checked by an unpolarized 670nm laser diode. Figure 3a shows the evolution of the first diffracted order as a function of time.

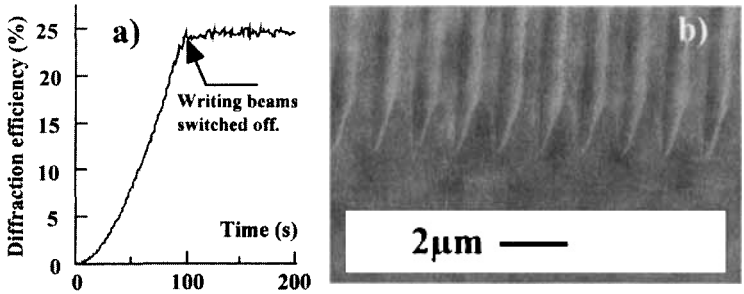
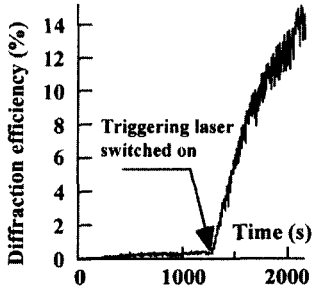


FIGURE 3 a) Evolution of the diffraction efficiency of the first diffracted order as a function of time ($I=100mW/cm^2$); b) Surface grating profile observed by SEM.

Figure 3b illustrates the surface profiles observed by scanning electron microscopy (SEM), revealing a regular surface relief grating with a phase shift of π with respect to the illumination pattern [11]. In these experiments, the highest diffraction efficiencies (~30%) were observed when the films were exposed to p-polarized writing beams. In the case of s-polarized writing beams, only an index volume grating with a weak diffraction efficiency (~1%) was inscribed. However, as illustrated in figure 4, the contribution of a third p-polarized writing beam triggers the deformation process.

FIGURE 4 Contribution of a third p-polarized writing beam to trigger the deformation process.



IV. NEAR-FIELD OPTICS -PRELIMINARY RESULTS

Experiments using near-field optical techniques were performed on these two systems in order to improve density data storage. A metallized tapered optical fiber tip was used as a subwavelength light source for the local discoloration of the dithienylethene sample (figure 5a). Preliminary results obtained on a 100 nm-thick sample show the near-field light transmission image in the vicinity of the discoloring spot (figure 5b). The rather large size of the discolored area (~650 nm) is probably limited by the sample thickness. Subwavelength discolored area has therefore not yet been achieved and thinner

samples are under investigation. Similar near-field experiments were performed on Azo-containing films. Photo-induced matter migration under the tip was observed. The topographic structure can be imaged in-situ with the same tip by the shear-force technique. As illustrated in figure 5c, structures of subwavelength size (40 nm large and 15 nm high) are easily achieved. Surprisingly, the tapered optical fiber tip does not need to be metallized probably because the mechanism involved in the matter migration does not only depend on the intensity distribution of the light source but also on the electromagnetic field polarization distribution. Note that, such an experiment corresponds to a density of binary recorded data as high as 400 bits.μm^{-2} (5Go.cm^{-2}).

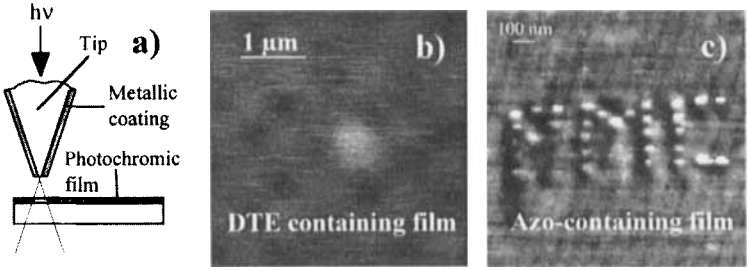


FIGURE 5 a) Scheme of coated tip, b) Discoloring spot, c) Acronym "PMC" written pixel by pixel.

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