

Reviews

Photochromic Sol–Gel Materials

David Levy

*Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, 28049 Madrid, Spain,
and Laboratorio de Instrumentación Espacial–LINES, Instituto Nacional de Técnica
Aeroespacial, I.N.T.A., Torrejón de Ardoz, 28850 Madrid, Spain*

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Among the many developments associated with sol–gel processing of particular relevance for information processing and optics applications is the preparation of photochromic sol–gel materials. If these materials are properly processed as thin films or attached to optical fibers, throughout the design of an adequate thermally and photochemically stable practical device, the properties of the light throughput may be modified. Hybrid organic–inorganic sol–gel matrixes or *ormocers* (organically modified ceramics) and *ormosils* (organically modified silicas) opened the gateway to approach to optical memory applications by either light or temperature writing and erasing on newly developed photochromic and thermochromic materials.

1. Introduction

A decade¹ has passed since the first photochromic molecule, *aberchrome 670*, served as a good illustration of what the organically doped sol–gel methodology can offer in the preparation of a silica gel photochromic material. The motivation was to develop novel materials for information processing and for other optics applications. Traditionally, photochromic glass preparations have been limited to a few dopants that can withstand the high temperatures of glass melting; by contrast, organic photochromism offers several tens of thousands of molecules with which one can tailor their applicability by the shade of color change, the direction of the photochromism, the rate of change in color intensity, reversibility, or unidirectionality (e.g., optical gates and information recording, respectively).

In this review, we emphasize some of the applications of photochromic doped sol–gel glasses performed in our laboratories, reviewing past results and describing recent progress, and summarize, to my knowledge, representative contributions related to this topic.

2. Entrapment of Organic Components into Sol–Gel Matrixes

Since 1984,² the sol–gel process has been used as a powerful method for the preparation of porous gel–glasses doped with organic molecules at relatively low temperatures (<150 °C), in which the organic molecular structures are not thermally damaged. Processing of organic doped sol–gel glasses for optics applications requires the precise control of compositional and pore surface variations in cage-trapped molecules. Incorporation of hydrophilic or hydrophobic dopants (e.g., optically active molecules) is done by solubilization in water or alcohol, respectively, or in the starting solution

used for the gel–glass (xerogel) preparation. The list of candidates that can be incorporated into inorganic or hybrid organic–inorganic sol–gel matrixes, *ormocers* and *ormosils* for optical or electrooptical applications,^{3,4} which are merely used as host matrixes containing active components, are almost unlimited. These include photochromic dyes, laser dyes, nonlinear optical dyes, liquid crystals, and biological or enzymatic functional molecules, etc.

Transparent SiO₂, Al₂O₃, TiO₂, *ormocers*, *ormosils*, etc., matrixes made by the sol–gel method are ideal as hosts for active organic dopants for several reasons: they are chemically produced at room temperature or slightly elevated temperatures, so that dopants can be introduced in the original sol and thus be easily entrapped within the pores of the gradually forming matrix and preserved without destruction; they are characterized by highly controlled purity, since they are synthesized of pure materials; they can be deposited as thin films or in any given shape according to the needed application; they are transparent in the whole visible range; they are porous, so they allow interaction of dopants with external liquids or gases, while at the same time sintering is unnecessary in various systems, since the dye molecules are not leached⁵ out the matrix cages by solvents. This virtually endless list of the valuable properties of these sol–gel matrixes warrant and explain the large and growing interest in research on these systems expressed, both fundamental and applied aspects, by the scientific community.

3. Photochromic Doped Silica Gel–Glasses

In principle, photochromic-doped sol–gel silica gel–glasses (SiO₂ gel–glasses) can be prepared by adding a photochromic molecule, e.g. a spiropyran photochromic dye, to a polymerizing solution of alkoxy silane monomers. To make possible these demonstrations, our first study concentrated on a number of the spiropyranes,⁶

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represented by 6-nitro-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline], abbreviated 6-nitro-BIPS (**1**), and its derivatives 5-bromo-8-methoxy-6-nitro-BIPS (**2**), 5-bromo-8-methoxy-5',6'-dimethyl-6-nitro-BIPS (**3**), 5'-chloro-5-bromo-8-methoxy-6-nitro-BIPS (**4**), and 5',6'-dimethyl-6-nitro-BIPS (**5**). Spectral changes, substituent effects describable in terms of the Hammett equation, and photochromic kinetic changes were studied in analyzing the response of the photochromic reaction to a continuously changing environment (environmental polarity and gradual change in the environment of the photochromic molecule) during the gel-glass preparation.⁶ A common observation for all the photochromic compounds used has been that photochromism (pm) changes gradually to reversed-photochromism (rpm) along the gel-glass formation (the stable forms in the dark are the colored ones, which could be bleached then by UV irradiation). These observations could be rationalized in terms of both, the geometrical and chemical changes in the environment of the photochromic molecule.⁶ At the first stage of the sol-gel reaction, the photochromic molecule is dissolved in the starting liquid solution (pm behavior). As the reaction proceeds, this situation gradually changes during the formation of the SiO₂ (wet gel) surface environment to an rpm behavior. During the gel drying stage, the molecular isomerizations and color change, as a result of UV irradiation, become restricted in the new solid environment (dry xerogel). This is a consequence of two considerable changes: first, the reduction in the size of the effective "free volume", which suppress the rotations; second, the photochromic material is stabilized by strong hydrogen bonds to the silanols of the silica cage in the SiO₂ gel-glasses (large spectral shifts). Under these conditions, the photochromic SiO₂ gel-glasses suffer from two problems: the photochromism was reversed (rpm) and, even more limiting, the photochromism stopped at the final dry xerogel stage.

Similar observations also resulted from the five 6-nitro-BIPS derivatives **1-5**, which were studied under the same reaction conditions. Moreover, the realization of a complete examination of the spectral changes upon irradiation and in dark conditions, demonstrated the ability of these photochromic compounds as excellent photoprobe molecules^{2,6,7} for the study of the sol-gel reactions characteristics, e.g., polarity, viscosity, and porosity, of the silica cage (SiO₂ cage). These experiments remarked the aggressive SiO₂-cage environment for the photothermal reactions of the embedded organic molecule, which in all cases results in a complete molecule degradation. The final material (dried xerogel) obviously could not have any practical applications.

Even spiropyrane and its derivatives have been largely used as doped molecules in silica gels;^{8,9} they were also reported in aluminosilicate gels. These authors pointed out that thermal reversibility of the photochromism as in silica gels was the main problem in becoming a thermally stable photochromic material. Additionally, it has been confirmed that photochromic spiropyranes doped in pure silica or in aluminosilicate matrixes lose their photochromic activity and/or change the direction of the photochromism (from normal photochromism to reversed photochromism).^{10,11}

3.1. Improvements to Silica-Gel Glasses. We have solved these problems by applying pore surface

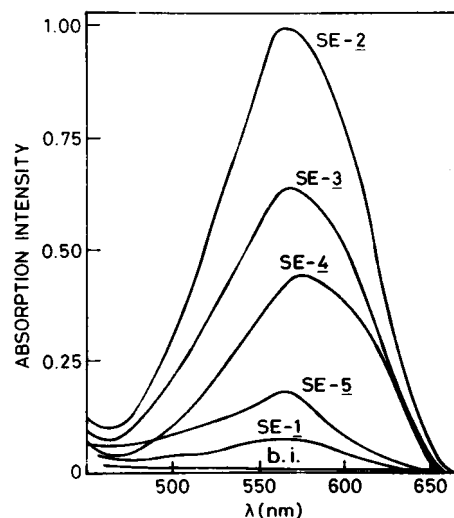


Figure 1. Absorption spectra of the silane-ethyl class (SE gel-glasses) of photochromic materials. The colorless baseline before irradiation (b.i.) is also shown (typical for all dyes). **1-5** refer to the five different derivatives of the 6-nitro-BIPS molecule.

variations in the inner SiO₂ cage of the SiO₂ gel-glasses, which contains the photochromic trapped molecules.⁶ A variation of the above-mentioned sol-gel method,¹² e.g., providing an organic phase on the silica surface by using additives (second phase) or by producing an ormocer (composed of organic functional groups on the silica cage), may offer the key for a successful and adequate opportunity to fabricate novel photochromic stable materials for practical applications. As a result, experimentation was conducted through two different strategies: First, we introduced the use of additives, acting as modifiers of the chemical properties (stabilizers) of the spiropyrane molecules, which were introduced as copolymer during the gel formation.¹² The variations in the cage composition of SiO₂ gel-glasses were performed by addition of poly(dimethylsiloxane)s (pdms, SP glasses), which induced sufficient flexibility into the matrix, allowing reversed photochromism in the final glass. The reversed photochromism in the SP glasses might be understood in terms similar to those of the SiO₂ gel-glasses, i.e., in the final gel-glass, the immediate environment is of Si-OH groups and is effectively affected by the use of the additive pdms.

The use of ormocers has been used as a second option for a successful and adequate preparation of photochromic materials. Specific ormocer gel-glasses doped with the same previous five 6-nitro-BIPS derivatives were obtained from silane-ethyl monomers, SE gel-glasses (apolar cage surface composed of Si-CH₂CH₃ groups).¹² Such surface composition does not stabilize the colored form of the trapped molecules; hence, normal photochromism is obtained. In SE gel-glasses, the grade of flexibility that is necessary to allow molecular rearrangements and rotations is obtained from the reduced cross-linking of this monomer in the final xerogel: only three of the Si bonds participate in the polymerization, compared to four in the pure SiO₂ gel-glasses.⁶ Therefore, the direction of photochromism, either normal or reversed, is controllable, and the photochromism properties remain in the final material with good chemical stability. Figure 1 presents the photochromic response after UV irradiation for a number of spiropyrane dyes

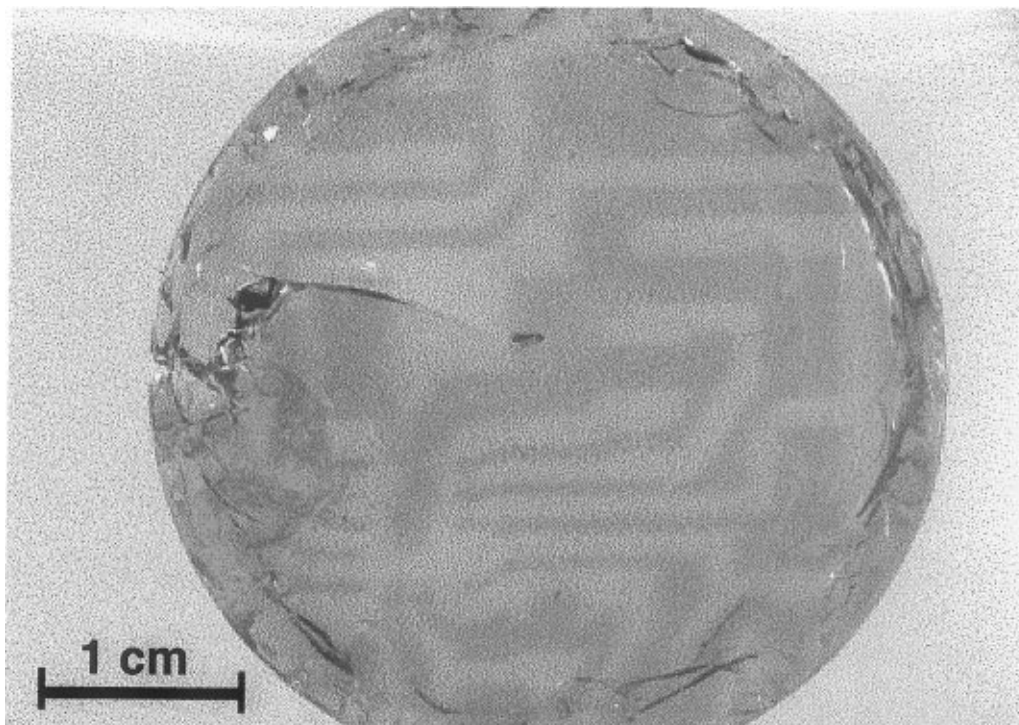


Figure 2. Demonstration of the information-recording ability of a SiO₂ gel-glass doped with 5-bromo-8-methoxy-6-nitro-BIPS. The cage surface is composed of Si-CH₂CH₃ groups.

trapped in SE-SiO₂ glasses. The gel glasses showed a normal photochromic behavior (Figure 2).¹²

An interesting work of Schaudel et al.¹³ evidenced that a very fast thermal bleaching can be observed in strongly hydrophobic matrixes. The authors introduced the *hydrophobic/hydrophilic balance* (HHB) of the hybrid matrix as an important factor, which controls the competition between direct and reverse photochromism. In the same context, Biteau et al.¹⁴ studied the competition between normal and reverse photochromism in two chemical organic and inorganic environments of the entrapping matrix cage and determined the kinetics of photodegradation through the excitation/emission spectra of fluorescent photoproducts of the spirooxazine molecules into doped gels.

3.2. Stability of Sol-Gel Photochromic Materials. An important feature regarding long-term technological or industrial applications of the photochromic materials is their thermal (chemical) and photochemical stability (fatigue). As mentioned above, the photochromic molecules are matrix environmental (cage composition) sensitive. Consequently, considerable effort in the preparation of new photochromic materials based on hybrid matrixes, using different photochromic compounds, is made on improving the preparation mechanism to obtain better products of superior stability. Extended work has been carried by the Ichimura group¹⁵ with azobenzene derivatives on the characterization of sol-gel bulk¹⁶ and thin-film¹⁷ materials, of different steric constraint due to modifications in the silica matrix, and by the fixation of the azobenzene to the silica gel matrix.¹⁸ Impregnation of the porous surface with an organic polymer^{18,19} was performed to improve the photochromic response as well as the fading rate, while keeping low levels of photofatigue and a high color stability.^{18,20} Improvements in this sense were also performed by the incorporation of new photochromic compounds as diarylethene derivatives,²¹ which do not

show thermal conversion below 140 °C. Other photochromic compounds that showed good thermal stability were the spironaphthooxazines both in pure silica gels and in hybrid silica matrixes. Thermal isomerization of azobenzenes in sol-gel glasses was described as being dependent on the amount of water on the silica surface,¹⁸ which is in concordance with previous results found by others authors, where hybrid matrixes enhanced the photochromic properties of the material.^{6,10,11,12,18}

Materials with high photochromic intensity and low photofatigue were found using perfluoroalkoxysilane derivatives or an imidazole derivative. Fluoroalkylsilane, bisphenol A, and methylimidazole can be also used as additives in the preparation of spirooxazine-doped photochromic organic-inorganic matrixes.^{22,23} The rigidity and the protective environment of these hybrid matrixes induce enhanced photochromic performances.

The physical properties obtained from a combination of sol-gel formulations have been used for the preparation of photochromic ormosil thin films for ophthalmic applications.²⁴ The reported films suffered from poor photofatigue resistance, through photochromism degradation via different mechanisms, which is related to the low dye concentration, the film thickness, and the lack of a protective environment.

Recently, Nakazumi et al.²⁵ introduced an effective method to increase the concentration of photochromic compounds in a gel film, consisting of a sol-gel coating solution containing malachite green leucocyanide in sol and superfine dispersed particles of a spiroopyran or spironaphthooxazine compounds, for which some forms of the colored photochromic species are stabilized in silicate gel films.

Although most of the photochromic sol-gel materials are based on photothermal rearrangements reactions and were prepared from spiroopyrane or spirooxazine derivatives, there are different physical and chemical

based photochromic behaviors that, usually directed toward a practical application, were adapted to a sol-gel matrix environment. Dai et al.²⁶ reported on a practical sol-gel material for optical and solar energy storage, based on the simple method of generating air-insensitive methylviologen radical cation in sol-gel glasses, which retains its blue color for months due to the restricted oxygen diffusion matrix. Optical chemical sensors for free metal cations in water and air, based on hybrid PMMA/silica thin films doped with 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide were also recently reported by Panusa et al.²⁷

4. Practical Photochromic Sol-Gel Devices

4.1. Optical Fiber Photochromic Device. In a recent application of doped sol-gel materials, it has been demonstrated that photochromic-doped sol-gel materials can be attached to optical fibers,²⁸⁻³⁰ the properties of the light throughput may be modified and can be optically processed. The sol-gel waveguide photochromic material can be easily formed. The fabrication process of the hybrid fiber device can be adapted to complicated configurations (they adapt themselves to the surface where the sol-gel material is deposited). The material shape can be modified upon manufacturing; the adopted shape is kept after the curing process. Once cured, these devices behave as optically addressed variable delay generators.

A simple fiber-optic/photochromic device²⁹ is made of two optical fibers placed in a V-groove removable connector with a small gap (50–500 μm) between the fiber ends, which is filled up with the photochromic material **1** (Figure 3). Silica gel-glasses obtained by the sol-gel process are chemically and optically very similar to the optical fiber itself. The matrix refractive index (1.453 at 633 nm) is quite close to the fiber core index (1.462); therefore, near index matching is achieved at the interfaces with the fiber ends. Losses were further decreased by careful preparation of the fiber ends. Therefore the Fresnel losses are drastically reduced, allowing the possibility of using doped sol-gel glasses for modifying the properties of the fiber light throughput. The doped waveguide is colorless before irradiation. External irradiation at 365 nm, which develops a reddish color in the photochromic dopant. Any optical signal sent through the fiber within the affected wavelength range will be therefore be attenuated accordingly. The color achieved with the UV irradiation in this material can be reversed with visible light within the absorption band, i.e., with the same optical signal attenuated by the colored material. The beam from the Ar⁺ laser is coupled to the optical fiber; the light cannot be transmitted through the gap until the laser light creates a waveguide through it by bleaching the photochromic gel-glass.

In Figure 4, the response of a sol-gel silica thin film doped with 5-bromo-8-methoxy-6-nitro-BIPS is shown for three rising cycles of the transmitted power of a 3 mm structure when an optical signal at 514.5 nm is applied at the input fiber.¹⁸ The final measured output power after each 225 s cycle is almost constant (–66.51, –66.31, –66.47 dBm, respectively). Material fatigue becomes apparent only after several hundred cycles (Figure 4 shows the output power for 1, 100, and 200 cycles). The UV irradiation period after each rising

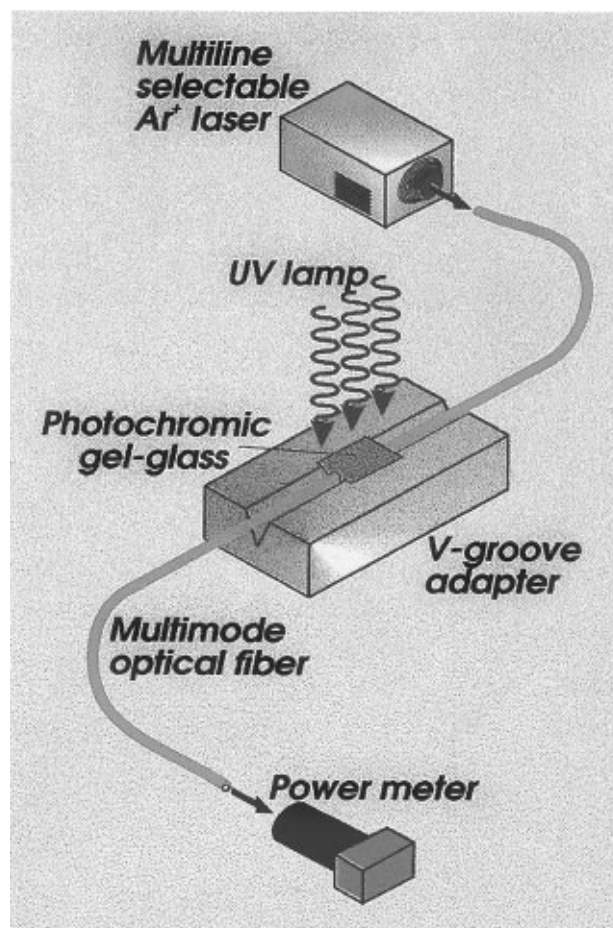


Figure 3. Experimental setup of a gel-glass optical fiber photochromic device.

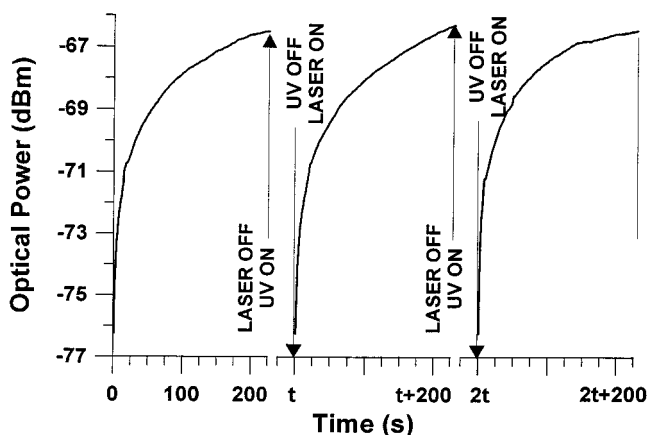


Figure 4. Three coloring/bleaching cycles of the optical gel-glass photochromic device.

cycle was 10 min. The time required for the waveguide to be formed depends on the gap width, the laser power, and the laser wavelength. In Figure 5, the response of the device is controlled by the input power. Figure 5 shows the optical output power for different input powers launched at 514.5 and 488.0 nm in a 3 mm gap. As expected, the higher the input power, the shorter the delay time. The delay also depends on the wavelength. The measured dynamic range varies from 15 to 33 optical dB for different input powers.

4.2. Thermochemical and Photochromic Memory Cells. The method of preparation of optical memories based on photochromic sol-gel systems¹² has been recently applied to the fabrication of new photochromic-

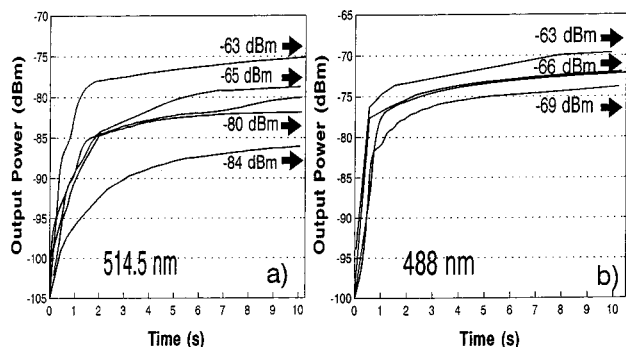


Figure 5. Optical output power time response of the optical fiber gel-glass photochromic device at room temperature for different input powers and wavelengths and for a gap length of 3 mm.

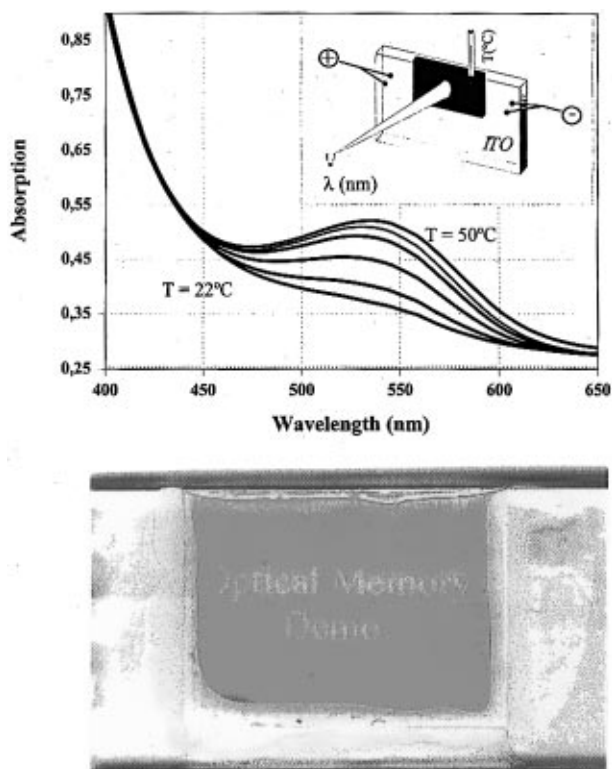


Figure 6. (a, bottom) Optical memory cell. (b, top) Photochromic behavior of 5-bromo-8-methoxy-6-nitro-BIPS with the temperature and the experimental setup for the characterization of the optical memory cell.

thermochromic materials with different stable states of distinct optical characteristics and light- or temperature-induced transitions between colored and colorless states.³¹ A thermochromic memory cell (Figure 6a), which consists of a rectangular transparent container with external surfaces coated with transparent ITO (heater) and a photolithograph, can be used as optical information storage media (Figure 6b). Coloration can be made either by exposure to UV light or by heat and writing (selective decoloration) by irradiation with an Ar⁺ laser at 514.5 nm.

5. Conclusions

The sol-gel process allows an easy method of preparation of optical memory systems and waveguides. Hybrid organic-inorganic matrixes, such as ormocers and ormosils, are the most effective candidates for the

preparation of nondegradable photochromic sol-gel materials. The doped sol-gel silica matrixes can be easily adapted to optical fiber devices. These systems allow the generation of different optical delays depending on the wavelength, optical input power, and waveguide length. This may be applied to the preparation of optical switches integrated in more complicated waveguiding and routing structures.

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