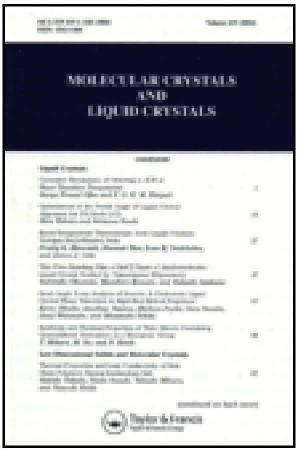

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Recent Applications of Photochromic Sol-Gel Materials

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RECENT APPLICATIONS OF PHOTOCHROMIC SOL-GEL MATERIALS

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Abstract

Among the developments associated with sol-gel materials, of relevance is the entrapment of photochromic molecules. Photochromic-doped sol-gel gel-glasses can be prepared by adding a spiropyrane photochromic dye to a solution of ethoxy silane monomers containing non-reacting ethyl radicals. After polymerization, normal photochromism (i.e., colored material upon UV irradiation) is obtained in the resulting matrix. The sol-gel matrix strongly affects the photo/thermal reactions of the embedded organic molecule. If these materials are attached to optical fibers, the properties of the light throughput may be modified. An approach to optical memory applications by writing and erasing on newly developed photochromic and thermochromic materials is reported.

In this report we emphasize on some of the applications of doped sol-gel glasses, reviewing past results and describing recent progress, mainly in our laboratories.

INTRODUCTION

Since 1984[1], the sol-gel process is being 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. Incorporation of hydrophilic or hydrophobic dopants[2] (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. Silica gel-glasses with adequate optical and photochemical properties, are good candidates for developing passive and active photonic waveguides for optical interconnections, where ruggedness, high chemical and thermal stability, low optical absorption in the visible and infrared range, and easiness of deposition on different substrates are often required. Processing of organic doped sol-gel glasses for optics applications requires precise control of compositional and pore surface variations in cage trapped molecules. Sol-gel glasses incorporating pH-sensitive dyes[3] were designed as potential substrates for fiber-optic chemical sensors, and are effective for use in instrumentation of long-term storage, durability and stability. Utilizing of the sol-gel process to the preparation of photochromic gel-glasses[4,5] by producing surface variations (e.g., providing an organic phase on the surface by using Si-CH_2CH_3 groups on the silica cage) may offer an opportunity to fabricate novel materials with practical applications.

PHOTOCHROMIC SILICA GEL-GLASSES

The first photochromic molecule which served as a good illustration of what the organically doped sol-gel methodology can offer in the preparation of a silica gel photochormic material was the Aberchrome 670.[6] The motivation was to develop novel materials for information processing and for other optics applications, and it serves as a good illustration of what the organically doped sol-gel methodology can offer: 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 the shade of color change, the direction of the photochromism, the rate of change in color intensity, reversibility (optical gates) or unidirectionality (information recording). To make possible these demonstrations (Figure 1), our study concentrated on a number of the spiropyranes, represented by 6-nitro-1', 3', 3'-trimethylspiro-[2H-1-benzopyran-2, 2'-indoline], abbreviated as 6-nitro-BIPS, and its derivatives.[4, 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 (SiO_2 glasses).[4] 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 accompanying changes in the photochromic molecule.[4] Upon the sol-gel reaction begins the molecule is dissolved in the starting liquid solution, which gradually changes to a SiO_2 surface environment. As the polymerization proceeds, molecular isomerizations as a result of irradiation become restricted in the new solid environment, .

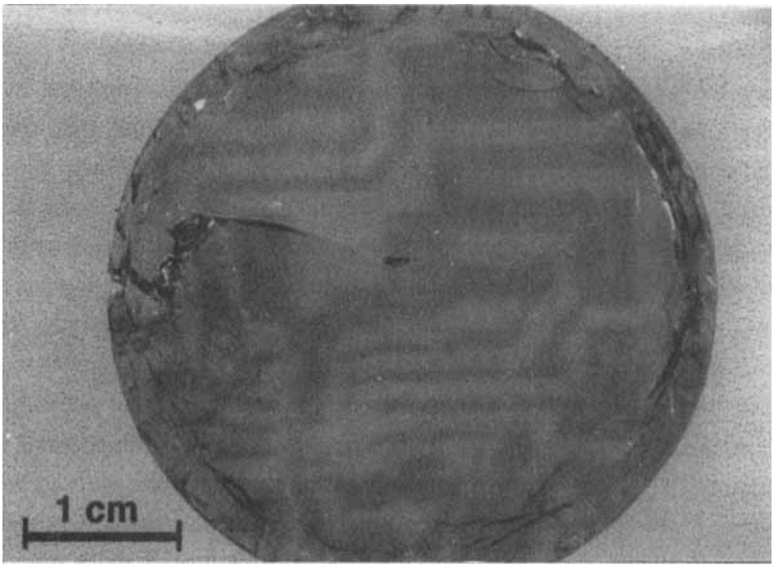

FIGURE 1. A demonstration of the information recording ability of a SiO_2 gel-glass doped with 5-bromo-8-methoxy-6-nitro-BIPS. The cage surface is composed of Si-CH_2CH_3 groups. (See Color Plate I).

This is a consequence of the reduction in the size of the effective "free-volume" for these rotations, and the photochromic material is stabilized by strong hydrogen bonds to the silanols of the silica cage in the SiO_2 glasses. Under these conditions, the photochromic SiO_2 glasses suffer from two problems: the photochromism was reversed and, even more limiting, the photochromism stopped at the final dry xerogel stage. The final material obviously could not have any practical applications.[4]

We have solved these problems by applying pore surface variations in the inner SiO_2-cage which contains the photochromic trapped molecules.[5] As a result, we have prepared silane-ethyl gel-glasses with an apolar cage surface composed of Si-CH_2CH_3 groups which do not stabilize the colored form of the trapped dye; hence, normal photochromism is obtained. In these gel-glasses, the grade of flexibility which is necessary to allow molecular rearrangements and rotations is obtained from the reduced cross-linking in the final xerogel: only three of the Si bonds participate in the polymerization, compared to four in the pure SiO_2 gel-glasses. Therefore, the direction of photochromism, either normal or reversed, is controllable; and the photochromism properties remain in the final material with good stability.[5]

IMPROVEMENTS TO SILICA-GEL GLASSES.

The spiropyranes and derivatives have been largely used as doped molecules in silica gels[7, 8, 9]. Also, aluminosilicate gels were reported as good host matrices for photochromic molecules[10, 11, 12]. These authors pointed out that, thermal reversibility of the photochromism in silica gels was the main problem to become a thermally stable photochromic material. Additionally, it has been confirmed that photochromic dyes doped in pure silica or in aluminosilicate matrices loose their photochromic activity and/or change the direction of the photochromism (from normal photochromism to reversed photochromism). Improvements in the photochromic properties of the silica doped gels have been performed both by modifications in the host matrix as well by the use of different photochromic compounds. Modifications in the silica matrix by the use of trifunctional silane precursors[7, 13, 14] or by the impregnation of the porous surface with an organic polymer[15] were performed to improve the photochromic response as well the fading rate, while were kept low levels of photofatigue[12] and a high color stability[13, 14]. Improvements in this sense were also performed by the incorporation of new photochromic compounds as diarylethene derivatives, which do not show thermal conversion bellow 140 C. It has been reported other photochromic compounds which showed good thermal stability[12-14], i.e. spironaphtooxazines both in pure silica matrix as in hybrid silica matrix. Thermal isomerization of azobenzenes in sol-gel glasses was described as dependent of the amount of water on the silica surface[15], which is in concordance with previous results found by others authors, where hybrid matrices improve the photochromic properties of the material[4, 5, 7-9, 13].

The matrix itself must be photochemically stable offering simultaneously a favorable environment to the photochromic dye. Efforts to improve the photochromic properties of the material were conducted through the incorporation of several additives to the silica matrix. Materials with high photochromic intensity and low photofatigue were found using perfluoroalkoxysilane derivatives or an imidazol derivative[10]. Other types of photochromic materials are being studied and preliminary results are very promising[14].

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[16,17,18], 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 fabricatio process of the hybrid fiber device can be adapted to complicated configuration (they adapt themselves to the surface where the sol-gel material is deposited). Th material shape can be modified upon manufacturing; the adopted shape is kept afte the curing process. Once cured, these devices behave as optically addresse variable delay generators.

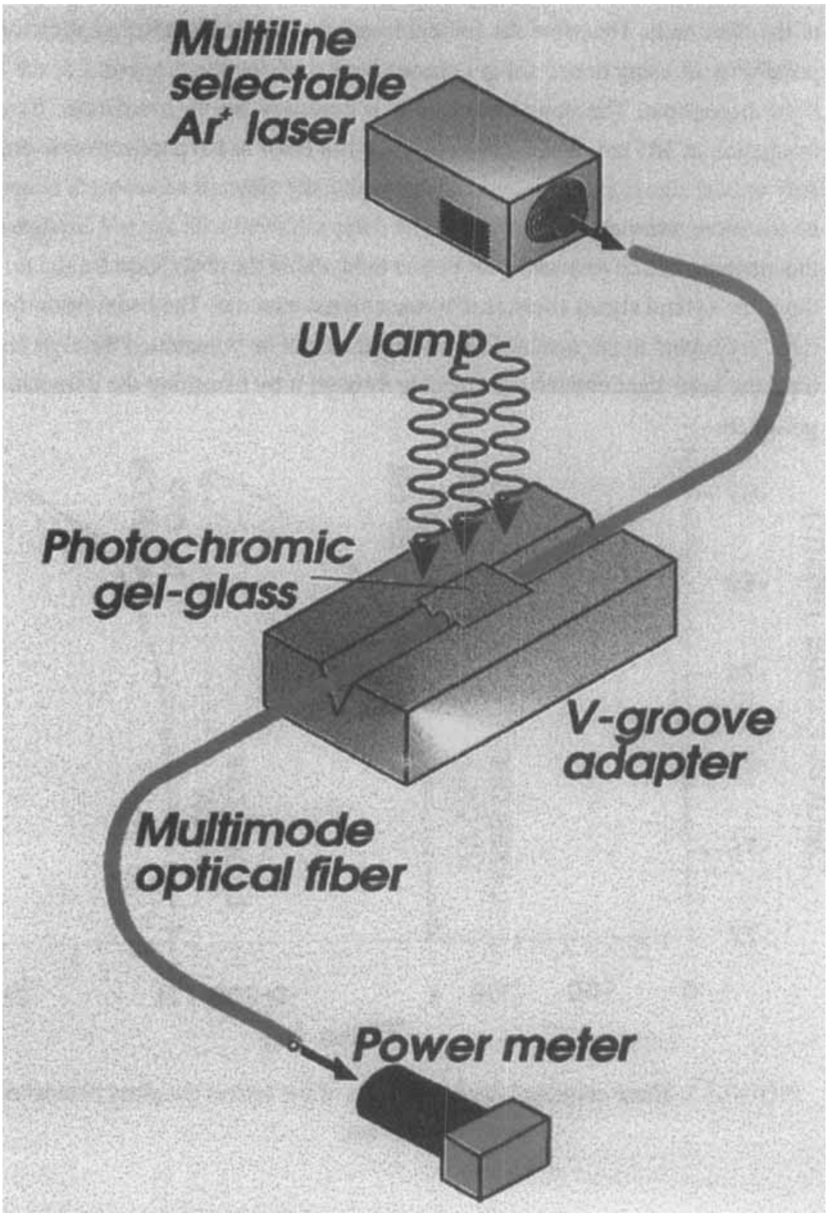

FIGURE 2. Experimental set-up of a gel-glass optical fiber photochromic device.

A simple fiber-optic/photochromic device[17] 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 (Figure 2). 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 nearly index matching is achieved at the interfaces with the fiber ends. Losses were further decreased by care 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 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.

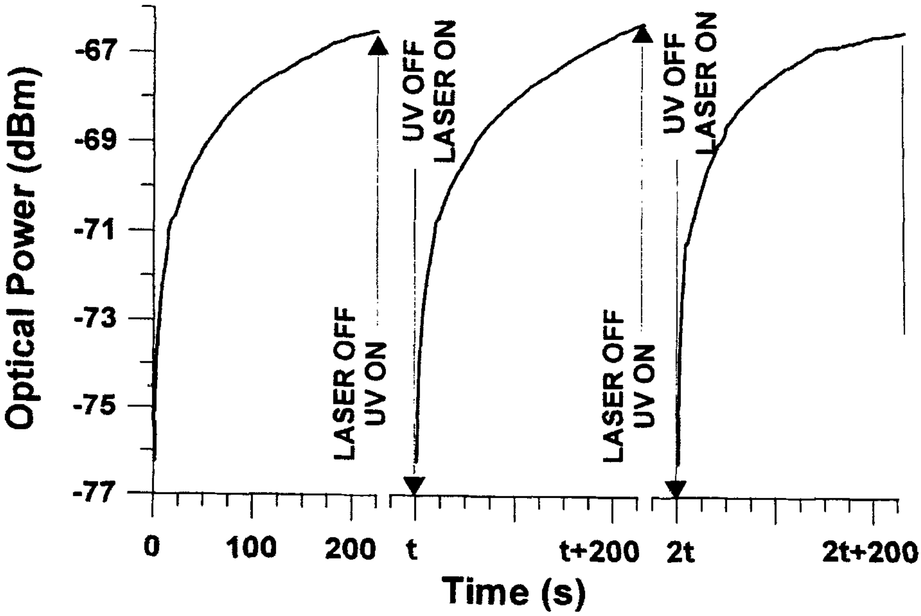

FIGURE 3. Three coloring/bleaching cycles of the optical gel-glass photochromic device.

In Figure 3, 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 3 shows the output power for 1, 100 and 200 cycles). The UV irradiation period after each rising cycle was 10 minutes. The time required for the waveguide to be formed depends on the gap width, the laser power, and the laser wavelength. In Figure 4, the response of the device is controlled by the input power. The Figure 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 is. The delay also depends on the wavelength. The measured dynamic range varies from 15 to 33 optical dB for different input powers.

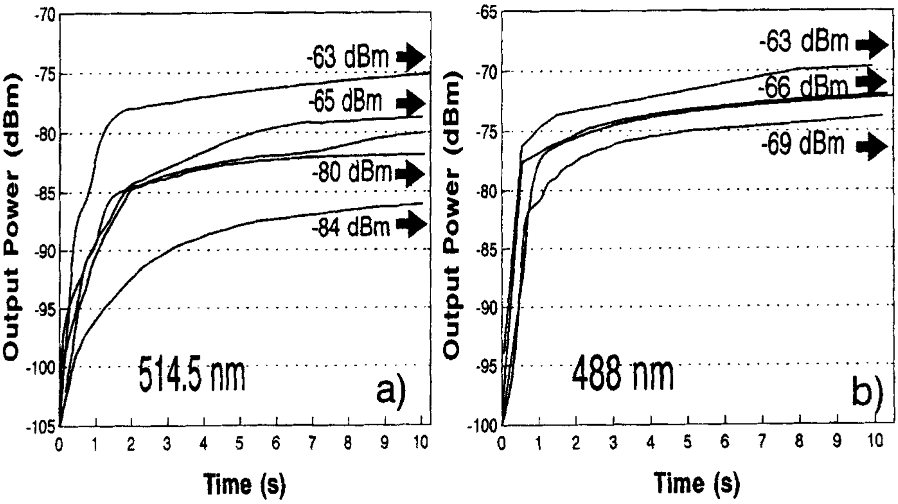

FIGURE 4. Optical output power time response of the optical fiber gel-glass photochromic device at room temperature for different input powers and wavelengths and for a gap length of 3 mm.

THERMOCHROMIC AND PHOTOCHROMIC MEMORY CELLS.

The method of preparation of optical memories based on photochromic sol-gel systems[5] has been recently applied to the fabrication of new photochromic-thermochromic materials with different stable states of distinct optical characteristics and light or temperature induced transitions between colored and colorless states.[19] A thermochromic memory cell, which consist of a rectangular transparent container with external surfaces coated with transparent ITO (heater) and a photolithography can be used as optical information storage media. 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.[19]

CONCLUSIONS

The sol-gel process allows an easy method of preparation of optical memory systems and waveguides. The doped sol-gel silica matrices 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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