

Nile Blue in Sol-Gel Films as a pH Optical Sensor

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ABSTRACT

Nile blue is incorporated into a "glass" prepared by the sol-gel method. Optical planar waveguides, formed by ion exchange in microscope glass slides, are used as sensing elements. Evanescent wave excitation is used to examine the behavior of the waveguide which is dipcoated with a thin layer of sol-gel within which the Nile blue is entrapped as a pH sensitive. The performance of the pH sensor is studied, showing higher sensitivity for higher values of pH.

1. INTRODUCTION

Optical sensors for chemical species are attracting considerable research interest mainly because of their potential for use in biomedical and environmental applications [1]. Many of these sensors rely on a change in the fluorescence or absorbance characteristics of a dye in response to changes in its chemical environment, e.g. pH or analytic concentration.

It is well known that a ray undergoing total internal reflection at a boundary between two dissimilar electric media produces an exponentially decaying (evanescent) field in the medium of lower refractive index. If the chemical species is within the evanescent field regions, and the wavelength is chosen to correspond on an absorption line of the species, then attenuation of the guided wave will occur.

The technique of some chemical sensors uses the evanescent field outside a waveguide, or a fiber core, to interact with the chemical species. This type of sensor has the potential for faster response over long interaction lengths and remote distributed sensing [2].

1.1. Sol-Gel Process

The sol-gel process is a method of preparing glasses and ceramics at low temperature by hydrolysis and polymerization of organic precursors [3]. Generally, it is concerned with the formation of inorganic oxides. The process typically involves a metal oxide, water, a solvent and frequently a catalyst, which are mixed thoroughly to achieve homogeneity on a molecular scale. Chemical reactions (hydrolysis and condensation polymerization) between the molecules lead to the formation of microscopic clusters in three dimensions, increased solution viscosity and, eventually, formation of a gel. This gel is essentially amorphous, porous material with the liquid solvents still contained within the pores. Low temperature curing expels all the liquids and leaves the porous oxide. Further curing at higher temperatures causes the pores to collapse and leads to densification of the material.

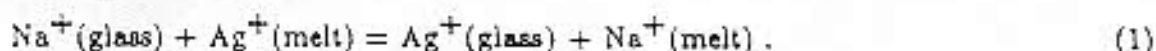
The prime technological importance of the sol-gel process is that it opens up a possibility of preparing homogeneous glasses and glass-ceramics at low temperature, that are hard to prepare by melting of oxide mixtures. Similar glasses are hard to prepare by melting oxides because of: i- the high melting temperature, and ii- the strong tendency to crystallize when cooling through the temperature having maximum crystallization rate. The sol-gel process is particularly suitable for coating deposition and fiber fabrication. Hence, the deposition of oxide coatings on substrates at low temperatures, and the fabrication of glass and glass-ceramic fibers are of potential technological importance. The sol-gel trapping technique offers also some other advantages over other heterogeneous systems for the study of photosensitized reactions: i- the medium is transparent and the method is simple as compared to, e.g., covalent attachment of the reactant to the glass. ii- with respect to absorbed systems, sol-gel trapping is free of disadvantages such as solvent-induced deposition by high ionic strengths.

1.2. Ion Exchange Giving a Waveguide in the Glass Surface

1.2.1. Theory

It is well known from glass technology that waveguiding layers can be produced at relatively low temperatures by means of ion-exchange process. In this process, a cation exchange is obtained by immersion of the sample in molten salts, sometimes in the presence of an electric field [4]. Many common glasses (i.e. window glass, microscope glass, ...) are known as "soda-lime" glasses, which indicates that they contain a certain proportion of sodium and calcium oxides in their silicon/oxygen network (typically about 12-14% Na_2O). The sodium ions are relatively mobile in the glassy network and may be replaced by certain other ions of the same valency. The ion exchange process is most easily performed by placing the glass specimen in a molten salt of the exchanging ion. For example, a silver nitrate or potassium nitrate melts.

The exchange process at the glass-melt can be represented by the equation:



An exchanged layer may thus be formed on the surface of the glass specimen and its thickness depends on the temperature of the melt and the time during which the sample remains in the melt. The presence of the silver in the exchanged layer raises the refractive index of the layer above that of the bulk (unchanged) glass. We thus obtain a thin (~few microns) region of higher refractive index sandwiched between regions of lower index. The bulk glass on one side and air (or sol-gel layer in our case) on the other. This arrangement forms a planar optical waveguide.

1.2.2. Fabrication

Much work for fabrication of optical waveguides was obtained by using silver-sodium (or potassium-sodium) ion exchange in glass [5-8] where pure silver nitrate melts were used as the source of silver ions, having the disadvantages:

1) A relatively large change in the refractive index is produced in soda-lime glass at its surface. For single mode operation of two dimensional guides with such a large index variation, channel widths of few microns only are necessary and so, their fabrication is very difficult.

2) High silver concentrations are present in the glass. The subsequent aggregation and nucleation of the silver atoms into colloidal crystals results in yellow staining of the glass, increasing guide loss, and making high-temperature fabrication unsuitable.

3) Silver nitrate is expensive.

These problems or disadvantages are overcome by diluting the silver nitrate melt with sodium nitrate, where no new exchange species are introduced [9]. Depending on the degree of dilution, the silver concentrations throughout the exchanged film can be reduced and the surface index change can be adjusted to any specified value between 0 and 0.09.

1.2.3. Determination of the Surface Index

To determine the surface refractive index, it is assumed that it is proportional to silver (or potassium) concentration and that at the glass surface all sodium ions are replaced by silver. To lower the surface index change to half its maximum value, only about 1% by weight silver nitrate in the melt is necessary. Although the diffusion temperature must be higher than that of pure silver nitrate melts (sodium nitrate melts at 307 °C), the lowering of the silver concentrations throughout the film reduces colloidal silver formation, giving excellent low-loss guides. The index profiles obtained can be modelled by a second order polynomial distribution combined with a reduction of the diffusion depth [9].

The prism coupling technique [4] is used, where a sufficiently narrow gap between the prism and the waveguide allows the field underneath the prism base to reach the waveguide and excite a waveguide mode. The width of the coupling gap must be extremely small for efficient coupling and the input beam must be positioned near the end of the prism.

The effective refractive index of the m th mode, n_{em} , as a function of its angle of incidence θ_m , can easily be obtained through the relation [4]:

$$n_{em} = n_p \sin \left\{ A + \sin^{-1} \left(\frac{\sin \theta_m}{n_p} \right) \right\} , \quad (2)$$

where A and n_p are, respectively, the prism angle and refractive index.

Assuming linear refractive index profile in the waveguide, its surface value, n_s , can be obtained, in the basis of Stewart et al. [9], as:

$$\frac{(2\pi/3\lambda) d (n_s^2 - n_{em}^2)^{3/2}}{n_s (n_s \cdot n_1)} = m\pi + \pi/4 + \phi , \quad (3)$$

where λ is the free space wavelength, d is the ion exchange layer (waveguide) thickness, n_1 is the slide glass refractive index, m is the mode number and ϕ is an angle given by:

$$\phi = \tan^{-1} \xi \left\{ \frac{n_{em}^2 - n_3^2}{n_s^2 - n_{em}^2} \right\}^{1/2} . \quad (4)$$

where ξ is constant ($= 1$ for TE modes and $= n_s^2/n_3^2$ for TM modes) and n_3 is the substrate refractive index.

2. PREPARATION OF SOL-GEL FILMS

To prepare the sol-gel films doped by the Nile blue dye, the following materials were used: tetraethoxysilane (TEOS Aldrich), ethanol, nitric acid, Triton X-100 (Aldrich) and deionized water; to the ratios 1 : 9.4 : 0.05 : 4.2. Fifteen drops of Triton X-100 were added to 25 ml of the mentioned solution. In order to assess the potential of the proposed technique for sensor fabrication, an absorbing dye was used as its absorbance is known to be a pH dependent. The Nile blue dye ($C_{20}H_{19}ON_3$) was chosen due to its absorption and fluorescence properties and because it is able to withstand the low temperature processing of the sol-gel glass without degradation. The Nile blue was added to the ethanol solution to give 10^{-5} and 5×10^{-5} M concentrations of the dye in the final sol-gel solution.

The absorbance of the final solution, as a function of the wavelength, was measured using the PERKIN-ELMER Double Beam Spectrophotometer in the visible range with a 1 cm cell. The results are displayed in Fig.1 for the two concentrations, showing a peak at $\lambda = 633$ nm, which represents one of the peaks of the Nile blue optical density (10).

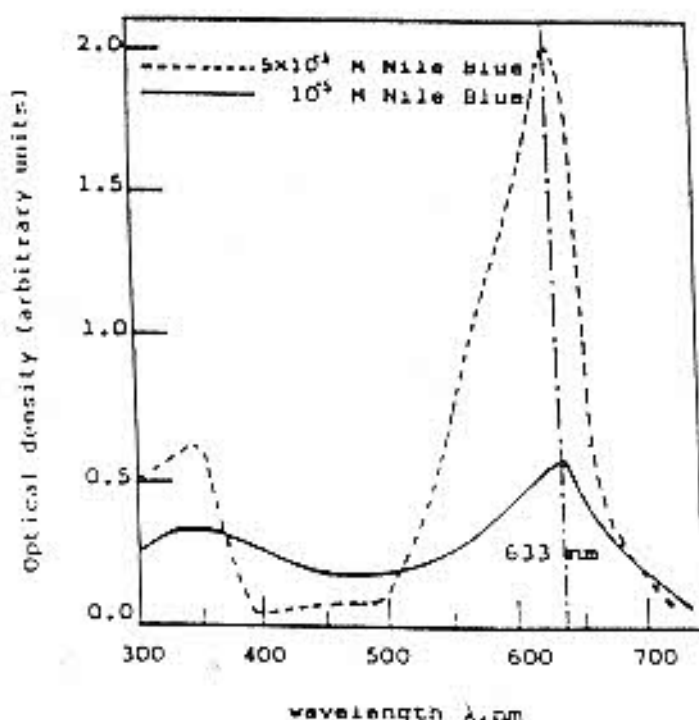


Fig.1 Absorbance spectrum of the Nile blue dye dissolved in the sol-gel solution for different concentrations.

The coating process of the microscope slides was performed by immersing the slides and withdrawing them from the doped sol-gel solution using a Gearbox for Precession d.c. Motor. The film was then air dried for 1 h. It was found that 15 times of immersion was suitable to give a flat and homogeneous film of thickness = $0.472 \mu\text{m}$, which was measured by the DEKTAK instrument. To study the sensor sensitivity, single mode slides

were used because they are easier and give more clear response than that of the multimode ones which were only used to determine the sol-gel refractive index. To reduce the sensor response time, the film thickness was chosen as small as possible, but to a limit that allows the evanescent field to pass through it.

3. EXPERIMENTAL ARRANGEMENT

The experimental set-up shown in Fig.2 was used to study the sensor sensitivity. A He-Ne laser, whose wavelength matches one of the absorbance peaks of the Nile blue, was used as an optical source and the transmitted signal was detected by a photodiode and its optical power was measured by a power meter. The laser output was effectively launched to the microscope slide through the prism coupling and the photodiode also was adjusted to receive the maximum input power. The slides used were multimode when determining the sol-gel refractive index and single mode ones when studying the sensor sensitivity and both are of the type having a waveguide layer made by diluting the potassium nitrate melt with the sodium nitrate.

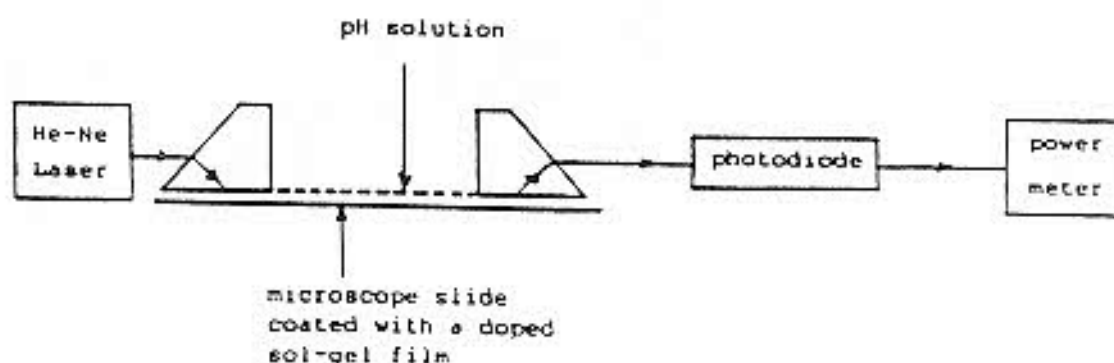


Fig.2 Experimental arrangement.

Different pH buffer solutions were used as an overlay for the sol-gel film then cleaned by water and air dried. These solutions were prepared according to the basis of A.I.Vogel [11], and the values of pH were calibrated using a pH meter.

4. RESULTS AND DISCUSSION

4.1. Sol-Gel Refractive Index

It is necessary to determine the sol-gel film refractive index in order to predict the sensitivity of the waveguide because if its value is near that of the substrate, a greater evanescent field will exist in the sol-gel film having more power and increasing the sensitivity.

First, we have determined the thickness, d , and the refractive index, n_3 , of the waveguide. A polarizer was used to separate the TM modes, and hence $\xi=1$, eq.(4). The angle θ_m was measured for two modes ($m=0,1$) for uncoated multimode slides, i.e. $n_2=1$ for air. The refractive indices $n_0=1.69$ for the prism, and $n_2=1.5125$ for the glass slide, together with the measured values of θ_m , are used in eq.(3), resulting in:

waveguide thickness, $d = 4.8582 \mu\text{m}$

waveguide ref. index, $n_3=1.5663$

The procedure was repeated using slides coated with the sol-gel film. The only change is that, assuming a fixed value for the sol-gel refractive index, the superstrate refractive index is $n_2 = n_{\text{sol-gel}}$ instead of air, giving an increase of 20-30 min in the mode angle, θ_m . The use of the obtained values for the waveguide thickness and refractive index, in eq.(3), gives $n_{\text{sol-gel}} = 1.38560$, in consistence with the value obtained by Givisbi et al. [12] for the same group of sol-gels.

4.2. Sensor Sensitivity

A He-Ne laser (633 nm) was used as an optical source to match one of the absorbance peaks of the Nile blue dye. The transmitted power, P_1 , for the coated slide was measured. Different pH buffer solutions were used as an overlay for the sol-gel film and the transmitted power in this case, P_2 , was measured for each value of pH. It was found that the value of the transmitted power increases when the pH solution is used. This is because the pH solution absorbs less power than air resulting in more transmittance of power.

The sensor sensitivity was studied through the ratio "S" between P_2 and P_1 . The results are shown in Fig.3 for 10^{-5} and 5×10^{-5} M Nile blue concentrations.

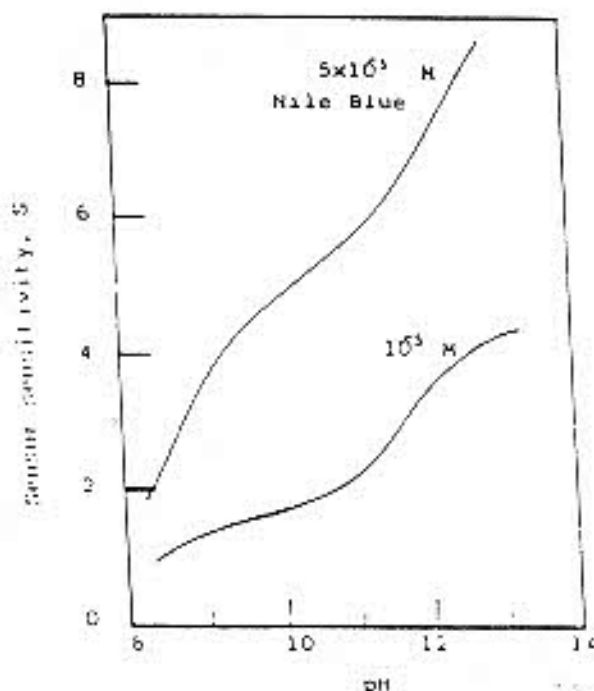


Fig.3 Variation of the sensor sensitivity, S, with the pH value for coated single mode planar waveguides at different dye concentrations.

From the obtained results for the red (He-Ne) light source, it is clear that the sensitivity increases with the increase of the value of pH . This can be explained as follows: as the lower pH buffer solution is colorless, it absorbs red light and hence, as the pH value increases, it goes from blue to red absorbing less red light, resulting in more transmitted power and increasing the sensitivity ratio. It is seen also, from Fig.3, that the sensor sensitivity increases for higher concentrations of the Nile blue dye because its absorbance is proportional to the concentration.

5. CONCLUSION

The use of porous sol-gel glass as a support structure for chemically sensitive dyes in optical waveguide sensors has been demonstrated. This technique offers the potential of fully distributed or quasidistributed multipoint sensing. Planar waveguide sensors formed by ion exchange in glass are recommended showing high sensitivity.

This technique has a number of important features which make it particularly attractive for integrated optic sensors:

- i- The low temperature processing allows environmentally sensitive dyes of low thermal stability to be used, like the Nile blue.
- ii- The compatibility of the silica sol-gel coating with the silica substrate of a planar waveguide results in a stable layer which is intrinsically bound to the substrate.
- iii- In the context of evanescent-wave devices, the porous sol-gel coating has a refractive index lower than that of the silica substrate, thereby providing proper guidance conditions.
- iv- The flexibility of the sol-gel processing technique allows the sensor designer to tailor the properties of the coating layer to the requirements of a particular sensor. An example of these properties is the refractive index which depends on the layer density and could be varied by the use of different ratios of the materials composing the layer, where the coating layer is the sensor in this case.

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