



Planar Integrated Optical Waveguide Sensor for Isopropyl Alcohol in Aqueous Media

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Abstract. An attenuated total reflection (ATR) sensor for water-miscible organic solvents was constructed using a combination of sol-gel processing and integrated optical waveguide (IOW) technologies. The sensor consisted of single-mode, sol-gel based planar waveguide coated with a 40 nm thick, porous sol-gel indicator layer prepared from methyltriethoxysilane and doped with methyl red. The response of the sensor to aqueous isopropyl alcohol (IPA) was investigated. Solvation of the indicator dye by IPA causes the absorbance spectrum to undergo a blue shift coupled with an increase in molar absorptivity. IPA was detected by measuring changes in ATR of the guided mode at 488 nm. A response curve extending from 1 to 100% (v/v) IPA in water was constructed for the sensor, from which a detection limit of 0.7% (v/v) IPA/water was estimated. Response and reversal times were typically less than one minute, making this sensor potentially attractive for on-line monitoring applications. The rapid response characteristics are attributable to relatively weak, reversible interactions between the indicator and analyte.

Keywords: attenuated total reflection (ATR), planar waveguide, chemical sensor, polarity-sensitive dye

1. Introduction

The detection of water-miscible organic solvents in process streams is critical to the semiconductor industry, which uses solvents, e.g. isopropyl alcohol (IPA),

for cleaning and drying operations [1]. At low concentrations in water, the detection of miscible alcohols such as IPA represents a very challenging chemical sensor problem because the key chemical and physical differences between the analyte and solvent are not large. For instance, IPA is fully miscible with water and boils within 20°C of water. Presently, mass spectrometry methods are frequently employed for the detection of non-volatile organic compounds in aqueous

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process streams [1]. While MS methods can provide part-per-billion (ppb) levels of detection under appropriate conditions, they can be costly to implement when multiple sampling sites in a single process stream must be monitored.

Alternate detection strategies include a recently developed amperometric sensor [2] for ethanol that relies on measurements of current produced by alcohol dehydrogenase (ADH) immobilized in a Langmuir-Blodgett (LB) film of stearic acid. Though the response time was found to be very fast (30 s) and the calibration curve exhibited linearity up to 500 μM ethanol, the stability of ADH was found to be problematic. Williams and Hupp [3] reported a sensor for alcohols and aldehydes based on the fluorescence of the cofactor nicotinamide adenine dinucleotide (NADH) co-entrapped with ADH in sol-gel monoliths. The sol-gel matrix stabilized the enzyme in inherently denaturing sample environments, such as organic liquids and the vapor phase. While aqueous ethanol concentrations from 10–1000 mM could be measured, the response time of the sol-gel monolith was very long (on the order of 1000 s). The high specificity characteristic of an enzyme, while providing exceptional sensitivity, limits the response of a catalytic biosensor to only a few target analytes (i.e. substrates of the enzymes).

Optical sensors that respond to a wider variety of analytes have also been reported [4–11]. For example, fiber optic sensors have been used to quantify ethanol [12] and other organic compounds [13] in aqueous solution by monitoring refractive index changes induced by differential swelling of the cladding. For ethanol, response times of about 1 minute were reported, with a linear calibration range extending up to 60% (v/v) ethanol in water (limit of detection not reported). Relative to MS methods, optical methods of detection are simple and potentially easy to implement at multiple sites over several process streams [14–16]. In addition to being inexpensive and non-destructive to the sample, measurements can be performed in situ and continuously, often with rapid and reversible responses.

Another option for optical transduction is the use of an indicator dye. The interactions of alcohols with indicator molecules, predominantly through hydrogen-bonding and hydrophobic effects, may produce changes in color, conductivity, redox potential, etc. For most dyes, these changes are minor and thus difficult to detect, given that water (the solvent) is a strong competitive interferant. However, the absorbance spectra of some organic dyes dissolved in

water are significantly altered in the presence of an alcohol [17–20]. This property has been exploited by several groups to develop optical sensor materials that respond to changes in solvent polarity [15, 18, 20–23]. This general strategy has been adopted here to create a rapidly responding, planar waveguide sensor for water-miscible organics, using IPA as a test analyte. Methyl red, a polarity-sensitive dye, is entrapped inside a thin, porous sol-gel film, which allows for rapid analyte exchange with the surrounding medium. IPA is distinguished from water on the basis of differences in very weak interactions with the dye. For signal transduction, the indicator film is deposited on a planar integrated optical waveguide (IOW) platform, containing integral grating couplers. IOW technology generally provides good sensitivity for probing very thin transducer layers [24, 25], such that rapid response can be obtained over a wide range of analyte concentrations.

2. Experimental

2.1. Waveguide Construction

The fabrication of integral grating couplers with a periodicity of ca. 400 nm in soda lime glass substrates (microscope slides, Gold Seal #3010) has been described previously [26, 27]. Two gratings, spaced ca. 15 mm apart, were etched into each substrate prior to deposition of the waveguiding layer. The Corning 7059 waveguide layer was sputter deposited onto the glass substrates, as described elsewhere [27]. The typical propagation loss was 1–2 dB/cm at $\lambda = 633$ nm. Waveguide layer thickness and refractive index were determined by measuring resonant mode coupling angles [28]; typical values were 400 ± 2 nm and 1.56, respectively.

2.2. Indicator (Transducer) Films

Methyltriethoxysilane (MTES, 2.00 ml) was hydrolyzed in the presence of concentrated nitric acid (0.20 ml) over 15 minutes, with continuous stirring. At the end of this time period, the warm, single-phase sol had cooled to room temperature. A methyl red (Aldrich) solution (50.0 ml), containing 0.46 mg/ml of indicator dissolved in 200 proof ethanol, was added to the sol and the mixture stirred for an additional 2 hours at room temperature. The sol was then aged quiescently for 48 hours at 4°C, prior to film deposition.

The sol-gel indicator film was deposited on the surface of the Corning 7059 waveguide by dip-coating, using a draw speed of 8.0 cm/min. The dip-coating was performed in an open laboratory, under ambient atmospheric conditions. Following dip-coating, the sensor was cured in air at 80°C for 5 hours. After cooling the sensor to room temperature, it was immersed successively in water, a 50-50 mixture of ethanol and water, and pure ethanol, for periods of 1 hour, 1.5 hours and 1.5 days, respectively. This 'pre-leaching' of the sensor indicator layer was performed to extract the loosely bound dye (the 'leachable fraction') from the film prior to use.

The thickness and refractive index of indicator films dip-coated on silicon wafers (111 orientation, p-type, 0.016–0.018 mm thickness) were determined using a Gaertner Scientific Model L116C ellipsometer to measure the amplitude ratio and phase change of 633 nm light reflected at a 70° angle. Iterative computations yielded index and thickness parameters, the latter value being constrained to ≤ 200 nm (this is a reasonable assumption based on the low viscosity of the coating sol).

2.3. Thick Sol-Gel Films for Investigation of Dye Response

Thicker (ca. 400 μm thickness, measured with calipers), indicator-doped sol-gel films were prepared to enable UV-visible spectra of the immobilized dye to be acquired with sufficient sensitivity (i.e. pathlength) with a single-pass transmission instrument (Hitachi U-2000). These 'thick' films, doped with methyl red, were used to evaluate the colorimetric responses of the dye to IPA and water as well as the ability of the incorporated dye molecules to resist leaching.

Tetramethylorthosilicate (TMOS 99+%, Aldrich) was hydrolyzed using a volumetric ratio of 71.4:4.7:1 of TMOS, water, and 0.048 M HCl. The water and dilute acid were premixed prior to addition of the TMOS, avoiding sudden mixing to preserve the two-phase system. The hydrolysis required ca. 50 minutes at room temperature, after which a single phase sol was obtained. Subsequently, 0.200 ml of ethanol containing the dissolved methyl red to be immobilized (at a concentration of ca. 6×10^{-4} M) was added to 0.300 ml of the hydrolyzed TMOS sol, and the mixture was homogenized. Finally, 0.200 ml of 0.02 M pH 6.2 phosphate buffer was added to the sol, and the mixture gently stirred for a few seconds. This last step was carried out in a disposable acrylate cuvet so that the mixture

could be gelled on one wall of the cuvet, when turned horizontally on its side and covered with Parafilm. The 'thick' film gelled within 20 minutes at room temperature. Films were aged for 18 hours at 25°C, prior to the introduction of the test solutions (IPA and water) to the cuvet.

Absorbance spectra of the doped thick films were acquired following 24 hour periods of soaking in water and, subsequently, IPA. The solvent containing dye that leached from the film was removed from the cuvet prior to spectral acquisition. UV-visible spectra were obtained using a double beam spectrophotometer, using a 'blank' (dye-free) sol-gel film in the reference beam.

2.4. Investigation of Sensor Response

The optical train used was similar to that of Yang et al. [24] for gaseous iodine sensing. The linearly polarized 488 nm line from an argon ion laser (Ion Laser Technology, Model 5500AWC) was modulated at 1.5 kHz using a chopper (Palo Alto Research, Model 300) and focused into a liquid flow cell (internal volume of 4.8 ml) mounted on a rotary stage. Laser light (incident power ca. 5 mW) was coupled into the waveguide through an incoupling grating on the sensor, with the incident angle (ca. 17.9° in water) selected to support the TE₀ guiding mode. After propagating down the waveguide, the light was outcoupled by the second grating coupler. The distance between the gratings (the sensor interaction length) was 15 mm. The outcoupled light was directed through an iris and a lens to a photodiode detector (Liconix, Model 40D). The photodiode output was sampled by a lock-in amplifier (Stanford Research Systems, Model SR830) referenced to the chopper frequency, after passing through a signal pre-amplifier (Oriel, Model 70710). The lock-in amplifier signal was sampled at 1 to 3 points per second using an A/D board (National Instruments) installed in a PC running Lab Windows software (National Instruments).

Solutions of various concentrations of IPA (99.9%, Aldrich) in water (Barnstead, 18.2 M Ω) were prepared and introduced either manually (with the aid of a syringe) or in a continuous flow through the cell (at 11.0 ml/min., using a peristaltic pump). The sensor response was determined at each different IPA concentration. The sensor response time (defined as the period required for the output signal to reach 90% of the total signal change) and detection limit were ascertained. All measurements were made at room temperature.

3. Results and Discussion

3.1. Characterization of Sol-Gel Layers

A number of indicator dyes was evaluated in an attempt to find a dye that: (i) exhibited a significant difference in spectroscopic properties when dissolved in IPA and water, and (ii) was sufficiently retained in a sol-gel layer upon immersion for extended time periods in water and IPA. Of the dyes that were sufficiently retained, only entrapped methyl red and Nile Red exhibited significant absorbance differences between IPA and water. Methyl red was selected over Nile Red because it exhibited a larger difference in molar absorptivity between the two solvents (see below).

Methyl red-doped, thick sol-gel layers were soaked sequentially in water for 1 hour, ethanol for 1.5 hours, and a 1:1 mixture of the two solvents for 1.5 days. (Previous work [29] has shown that this time period is sufficient to extract the 'leachable fraction' of dye molecules entrapped in a hydrated monolith). Absorbance measurements performed before and after the soaking procedure showed that approximately 30% of the methyl red present in the sol at gelation was retained. The 'leachable fraction' was therefore ca. 70%. Based on this measurement, the effective molar concentration of methyl red in the indicator layer of the sensor was estimated to be $490 \mu\text{M}$, corresponding to 3×10^{17} molecules per cubic centimeter.

The pH in the pores of a silica sol-gel is ca. 4 to 6 [30], and the pK_a of methyl red is ca. 5 [31]. Although the exact mechanism is unclear, these data suggest that methyl red retention in a hydrated TMOS gel can be partially attributed to electrostatic attraction of the dye to the pore walls. Other potential contributors include hydrophobic interactions between the dye and surface methyl groups (in an MTES indicator film) and hydrogen bonding of the dye to surface silanols.

The molar absorptivity of methyl red dissolved in IPA is nearly 1.5 fold greater relative to the dye dissolved in water; the increase in absorptivity is accompanied by a blue shift in the spectrum (data not shown). This solvatochromic behavior was also observed for methyl red entrapped in TMOS. In Fig. 1(a) are shown absorbance spectra of a methyl red-doped, thick sol-gel layer, acquired after soaking in water for 24 hours (curve A) and after soaking for an additional 24 hours in pure IPA (curve B). The spectrum showed a blue shift and increase in molar absorptivity upon equilibration of the film in IPA, relative to water. The difference spec-

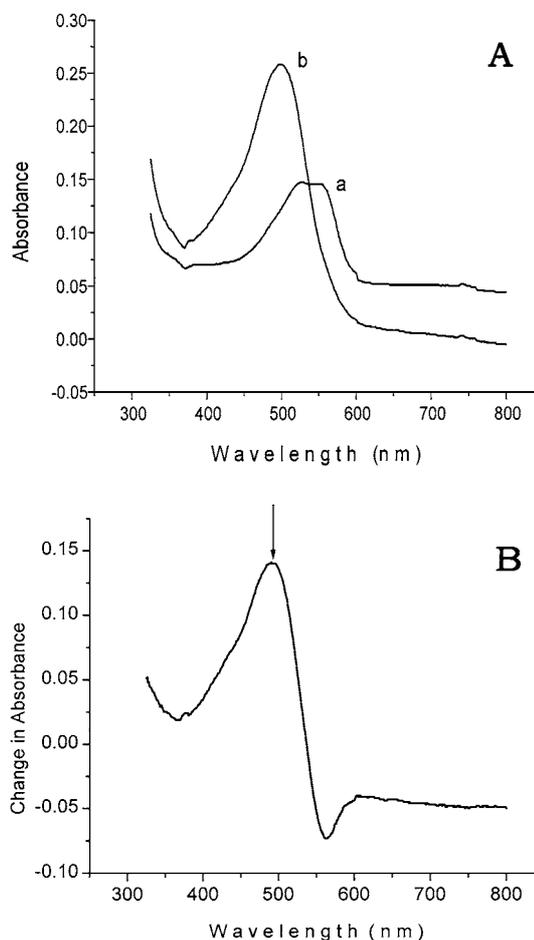


Figure 1. (A) Effect of IPA on the absorbance spectrum of methyl red (1.7×10^{-4} M) immobilized in a TMOS sol-gel monolith (0.4 mm thick). To a pre-leached gel equilibrated with water (spectrum a), 100% IPA was introduced and equilibrated for 24 hours (spectrum b). (B) The difference spectrum (b-a) shows that the maximum (ca. 1.5-fold) increase in absorbance (ca. 1.5-fold) occurs at 491 nm (arrow).

trum (Fig. 1(b)) shows that the maximum absorbance change occurred at 491 nm. Thus the response of entrapped MR to varying IPA:water mixtures can be readily probed by using the 488 nm line of an Ar ion laser. The lower $S_1 \leftarrow S_0$ transition energy observed for MR in the water-equilibrated monolith is attributed to an enhanced ability of the more polar water molecules to stabilize the excited state of the dye, relative to IPA molecules [25].

Dye-free, thin MTES films were deposited on Si wafers to enable the optical thickness of the indicator layer to be measured. Ellipsometry yielded a refractive

index and thickness of 1.43 and 40 nm, respectively. A thickness of 40 nm was thought to represent an appropriate compromise between sensor sensitivity and response time. The evanescent depth of penetration (d_p) of the Corning 7059 waveguide used for sensor construction is approximately 100 nm [25], and sensor sensitivity would be enhanced by using an indicator thickness approximately equal to d_p . However, a thinner indicator layer was employed here to provide a rapid sensor response time for the analyte dissolved in aqueous solution, in which diffusion is significantly slower than in the gaseous media interrogated using a sensor of similar design [25]. We also note that using the trifunctional precursor MTES produces an indicator layer film of adequate durability (mechanical hardness) and high porosity, relative to a more highly crosslinked material such as that obtained using a tetrafunctional precursor such as TMOS [24].

3.2. Sensor Response to IPA

Example data from the evaluation of sensor response to IPA/water mixtures are shown in Figs. 2 and 3. The raw change in outcoupled light intensity due to injection of 10% (v/v) IPA/water, followed by 100% water, is shown in Fig. 3. Using a constant flow rate of

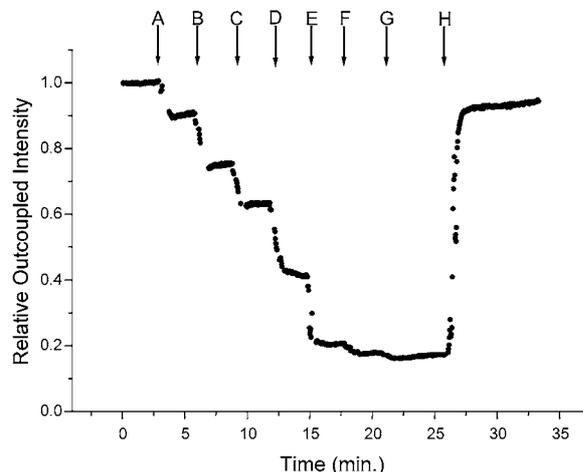


Figure 2. Outcoupled light intensity from the sensor when exposed (successively) to (A) 1%, (B) 5%, (C) 10%, (D) 20%, (E) 50%, (F) 75%, (G) 100% and (H) 0% v/v IPA/water. Each solution change was effected by manually injecting a total of 18 ml into the flow cell, every ca. 2.5 minutes. Note that the last injection (H) was not sufficient to flush all of the IPA from the flow cell (leaving ca. 1% v/v IPA in the cell); however, complete reversal of response was achieved with the injection of an additional 10 ml of water (not shown).

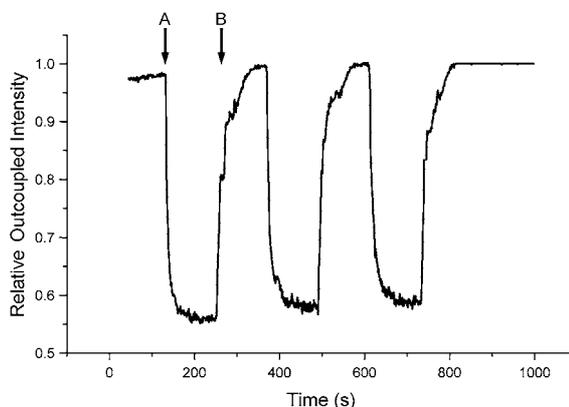


Figure 3. Outcoupled light intensity from the sensor when exposed successively to solutions containing 10% v/v IPA/water and pure water, a total of three times each. At time A, IPA solution was introduced into the flow cell (flow rate = 11 ml/min.); at time B, the cell was flushed with pure water. Laser drift is believed to be responsible for the slight, systematic 'up-slope' of the sensor response. The response after 800 s shows the inherent optical noise level in the measurement, after removal of flowing solution from the cell.

11 ml/min in a cell volume of 4.8 ml, the response and reversal times were 12 and 57 seconds, respectively. The rapid response characteristics are attributable to relatively weak, reversible solvation of the indicator by IPA.

Although the dynamic range of the sensor spanned <1% to 100% v/v IPA/water (Fig. 2), the sensitivity to IPA was found to be maximized at the lower concentrations. A plot (Fig. 4) of the absorbance at 488 nm versus concentration of IPA yielded a calibration curve which could be fit by a first order logarithmic equation. The non-linear calibration curve is likely due to the combination of a spectroscopic shift and accompanying increase in the absorptivity, upon (preferential) solvation of the immobilized dye by IPA, relative to solvation by water. From the calibration plot, and an estimated minimum detectable absorbance of 0.003 a.u., a limit of detection (LOD) of ca. 0.7% (v/v) IPA in water was calculated for the sensor. During the evaluation of sensor performance, the device was exposed to over 60 liters of various solvents, without degradation in the response characteristics illustrated in Figs. 2–4. Thus any effects of slow leaching of methyl red on long-term sensor performance were minimal.

The sensor response to organic solvents other than IPA was also investigated. The absorbance measured in response to injections of 10% (v/v) solutions of IPA, ethanol, methanol, acetonitrile, and acetone into the waveguide flow cell is shown in Fig. 5. The smaller

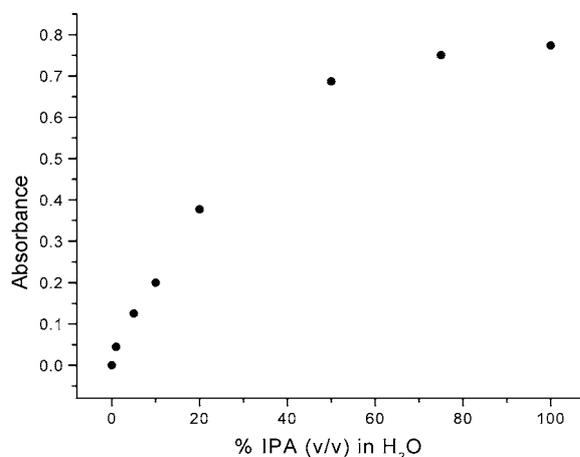


Figure 4. Calibration curve of absorbance (at 488 nm) measured as a function of IPA concentration, derived from the data in Fig. 3. The solid line represents a first-order logarithmic fit of the data ($\chi^2 = 6.7 \times 10^{-4}$), with an exponential decay constant of 27.2 ± 1.8 (% v/v), a pre-exponential factor of -0.78 ± 0.01 a.u., and a y-intercept of 0.77 a.u. Error bars were typically smaller than the size of the data points, and thus are not shown.

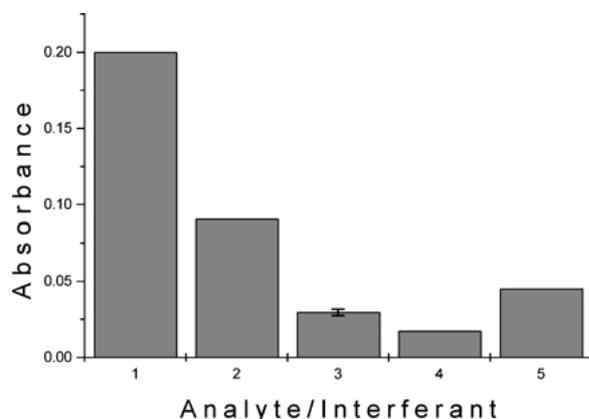


Figure 5. Comparison of sensor response to several organic solvents. A 10% (v/v) solution of each solvent dissolved in water was injected sequentially into the flow cell and the steady state absorbance was measured at 488 nm (1 = IPA, 2 = ethanol, 3 = methanol, 4 = acetonitrile, 5 = acetone).

optical response of the sensor to the more hydrophilic methanol and ethanol (relative to IPA) is an expected result, given the polarity-sensitive nature of the entrapped indicator. Acetone and acetonitrile also generated absorbance changes less than observed for IPA. Overall, the relative responses are inversely correlated with the dielectric constants for the solvents, which are 80, 36, 33, 24, 21 and 18 for water, acetonitrile, methanol, ethanol and acetone and IPA, respectively [32]. Thus,

as the dielectric constant of the solvent decreases, the extent to which the solvent molecules stabilize the excited state of methyl red is reduced, which generates a lower sensor transmittance at 488 nm (relative to pure water). Although the magnitude of the sensor response is largest for IPA, the nature of the transduction mechanism clearly precludes obtaining a selective response in the presence of other organic solvents. In other words, the sensor responds 'universally' to polar organic solvents dissolved in water, which makes it potentially useful for on-line monitoring of total organic solvent content in aqueous process streams.

4. Conclusion

An optical chemical sensor that rapidly responds to IPA dissolved in water, with a limit of detection of ca. 1% v/v, has been constructed. The high sensitivity of this device is characteristic of the single-mode, planar IOW transducer platform, which is amenable to probing small optical changes in thin films. The rapid response is ascribed to the use of a combination of a thin indicator film, made porous through sol-gel processing, and a transduction mechanism based on relatively weak, reversible solvation of the indicator by IPA. The reproducibility in sensor response upon repeated exposure to solvents shows that indicator leaching did not adversely affect device performance. Preliminary results (data not shown) indicate that the sensor performance is maintained even after 6 months of storage in the dark in air. However, the polarity-sensitive mechanism by which the entrapped MR responds to the analyte also generates a response in the presence of water-miscible organic solvents other than IPA. Thus this first-generation device may be applicable to detection of total water-miscible organic solvents in an aqueous process stream. As presently constructed, the broad dynamic range of response (<1% to 100% v/v IPA) makes this device potentially useful for applications in which the organic solvent content is several percent or higher (e.g. determination of ethanol in the beverage industry).

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