New optical sensor for volatile organic compounds (VOC) using birefringent porous glass

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Abstract
Changes observed in polarized light transmission through an anisotropic material, such as birefringent porous glass, upon contact with air bearing vapors of volatile organic compounds serve as the basis for a very sensitive broadband chemical sensor. When properly designed, vapor sensors based on such porous glasses show changes in intensity or spectral content (color) detectable by eye. When placed between two crossed polarizers the form-birefringent porous glass produces an observable phase shift that undergoes a readily detectable decrease upon exposure to all organic vapors we tested thus far. The optical effects resulting from exposure to vapors are reversible and believed to result from capillary condensation of solvent vapors and attendant reduction of anisotropy. A good control of the microporous structure as well of the surface chemistry offers flexibility for tuning the sensor response to VOC industrial applications. Simple sensor miniaturization with low cost materials is possible.

Keywords
Microporous silica structure, capillary condensation, birefringence, optical anisotropy, phase shift, chemical sensor.

INTRODUCTION
Increasing interest for VOC detection and recent progresses with birefringent porous silicon [1] prompt us to report our own work on birefringent porous glass for vapor-sensing applications. We present here a simple optical design consisting of a birefringent porous glass [2] placed at 45° between two crossed polarizers separating the light source and the light detector which could be electronics or naked eye.

MATERIALS AND METHOD

Porous glass preparation
A borosilicate glass was produced in order to shape a rod preform which was drawn into fibers. Glass fibers were then heat treated for several hours in order to induce a spinodal decomposition leading to phase separation. The boron rich phase was leached out by acid treatment in order to produce a silica rich interconnected porous structure [3]. Fibers were then rinsed in water and isopropanol and were stored under vacuum at room temperature. The fibers were two side polished to obtain a desired thickness.

Porous glass characterization
Nitrogen porosimetry was performed using a Coulter Omnisorp™ 100 Brunauer-Emmett-Teller (BET) system. The samples were pre-treated at 150ºC for 2 h before measurements in order to remove adsorbed molecules (such as water vapor). Scanning electron microscopy (SEM) imaging was performed at 15 kV using a JEOL-840-A microscope. Freshly fractured samples were made conducting by sputtering a thin layer of Au/Pd.

Sensor set-up
For optical measurements, the porous samples were placed inside a closed stainless steel cell at 45º between two crossed Glan-Thompson polarizers. The porous fiber was illuminated using a halogen lamp and the light passed through the polarizers was analysed using an Ocean Optics SD 2000 fiber optic UV/Vis spectrometer. The cell was subjected to a continuous 1 L/min flow of either dry nitrogen with or without organic solvent vapors. The concentration of the organic vapors was controlled by injecting in an inline heated mixing cell liquid solvents using a PHD 2000 Harvard Apparatus programmable microinjecting syringe pump. The experimental set-up is described in Figure 1.

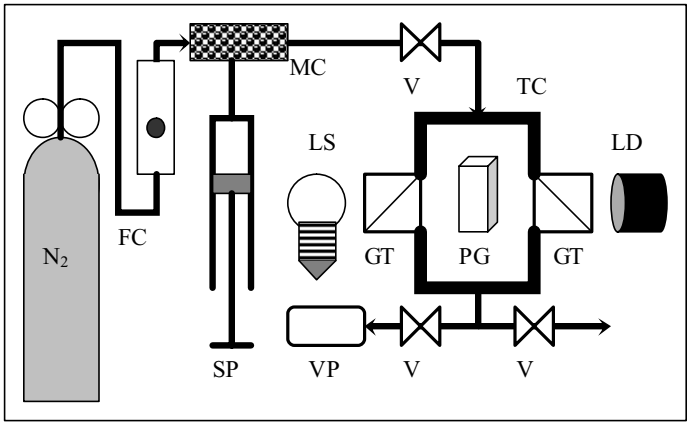

Figure 1 : Experimental set-up. FC: Flow Control, SP: Syringe Pump, MC: Mixing Cell, TC: Test Chamber, LS: Light Source, GT: Glan-Thompson polarizers, PG: Porous Glass, LD: Light Detector, VP: Vacuum Pump, V: Valve

THEORY

When the optical axis of the birefringent fiber is placed in the propagation plane (normal to the propagation axis) preferably at 45° with respect to the linear polarization direction, the electrical field vector $\vec{E}$ of linear polarized light is decomposed in two orthogonal projections E_x, E_y along the ordinary (n_o) and extraordinary (n_e) refractive indexes. Due to birefringence, each projection of the electrical field vector experiences a different refractive index and thus a different light path resulting in a phase shift $\Delta\phi$ between the two projected components of the electric field vector. At a given wavelength λ, the phase shift $\Delta\phi$ is given by:

$$\Delta\phi = \frac{2\pi \cdot d \cdot \Delta n}{\lambda} \qquad (1)$$

where d is the thickness of the birefringent sample and $\Delta n = n_e - n_o$ is the birefringence.

The linear analyzer is preferably crossed (e.g. at 90°) with the polarizer to make sure that the only light passing through the analyzer is light that has been rotated by the birefringent sample. The analyzer transmits along its axis of polarization the components of the two phase shifted projected electrical field vectors that experienced different optical paths.

For a uniaxially birefringent material, the output intensity $I_{Out\perp}$ for 90° crossed polarizers at a given wavelength λ is given by:

$$I_{Out\perp} = \kappa \cdot \frac{I_{In}}{2} \cdot \sin^2\left(\frac{\pi}{\lambda} \cdot d \cdot \Delta n\right) \qquad (2)$$

where κ is a positive factor (< 1) that takes into account all the power losses such as partial reflections and possible diffusion along the optical path, I_{In} is the source intensity and other terms are defined above.

In such conditions, maxima of transmission occur when:

$$d \cdot |\Delta n| = \frac{2m+1}{2} \cdot \lambda \qquad (3)$$

where m = 0, 1, 2, … and minima of transmission occur when:

$$d \cdot |\Delta n| = m \cdot \lambda \qquad (4)$$

The transmittance spectrum depends thus on the thickness d as well as on the birefringence Δn of the birefringent material.

RESULTS

Using the Brunauer-Emmett-Teller (BET) nitrogen porosimetry, the surface area of the produced porous glass fibers was found to be about 350 m²/g with a pore diameter distribution ranging from 2 nm to >60 nm and an average pore maximum diameter of about 3.5 nm.

Scanning electron microscopy (SEM) micrographs of freshly fractured glass fiber surface showed the presence of an interconnected porous structure as illustrated in Figure 2.

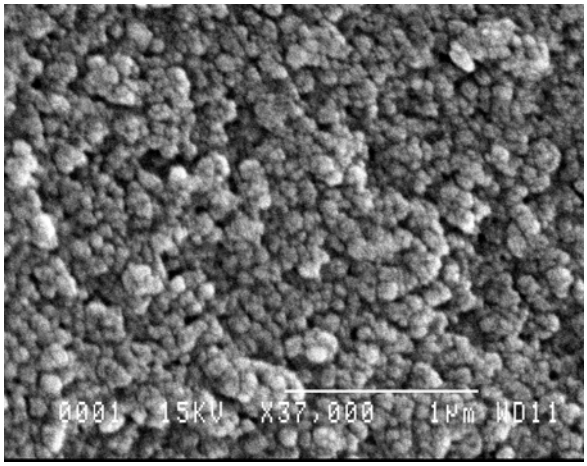

Figure 2 : SEM of the birefringent porous glass (× 37 000, horizontal bar is 1 µm)

A polished birefringent porous glass fiber was oriented at 45° between two crossed polarizing Glan-Thompson polarizers. The light from a halogen source passing through the sample was analyzed using an optical fiber UV/Vis spectrometer. A 300 µm thick polished porous glass sample (not shown) had a transmission minimum around 440 nm and a maximum around 850 nm whereas a 600 µm thick sample (see Figure 3) had two minima around 460 nm and 880 nm and a maximum around 600 nm. From such experimental results and assuming a uniaxially birefringent material, a birefringence of about $|\Delta n| = 1.5 \cdot 10^{-3}$ could be estimated for the porous glass sample.

It is believed that for this glass the optical anisotropy may be related to the combinatory effect of the anisotropic shape of the pores with the orientation of secondary silica gel strata deposition occurring during the leaching step [4].

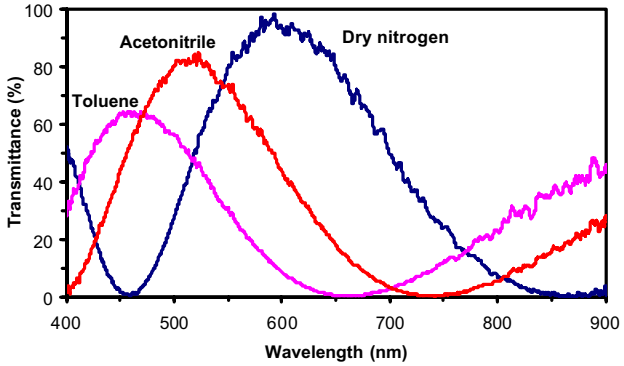

Figure 3 : Shift of the transmittance spectra of birefringent porous glass fiber in presence of acetonitrile and toluene (1000 ppm in dry nitrogen at 1 L/min). The glass sample is oriented at 45° between two crossed Glan-Thompson prisms

Interestingly in the presence of chemical vapor substances such as VOC, the birefringence is reduced and the transmitted spectrum is thus shifted towards the smallest wavelengths making this phenomenon potentially interesting for the development of a new kind of optical sensors for VOC detection.

As shown in Figure 3, two organic solvent vapors are easily detected at 1000 ppm (in a nitrogen flow of 1 L/min). Acetonitrile (n_D 1.344, B_p 81-82°C) induces a dramatic shift of the transmission maximum from ~600 nm for dry nitrogen, down to ~515 nm ($\Delta\lambda = 85$ nm). For toluene (n_D 1.496, B_p 110°C) which condenses more easily inside the porous structure, the shift of the transmission maximum is even greater at ~460 nm ($\Delta\lambda = 140$ nm). In both cases it has been observed that the shift is concentration dependant.

The condensation of the organic vapors into the porous structure usually induces a reduction in birefringence. A reduction in total transmitted light is also observed probably due to increased light diffusion by the sample as different pore size domains from the outside to the inside of the porous sample are filled and due to an increased total effective index of the porous glass as solvent vapors ($n > 1$) take the place of air ($n \sim 1$) in the pores. It should be mentioned that the increase in light diffusion caused by the solvent could be a transitory phenomenon or not, depending on the porous structure of the glass, and may be due to the creation of localized condensed vapors whose domains sizes are comparable to the size of the wavelengths and which may thus give rise to optical discontinuities [5]. Such phenomenon could be used in conjunction with phase shifting to increase the sensitivity of detection in cases where decreased light intensity is observed.

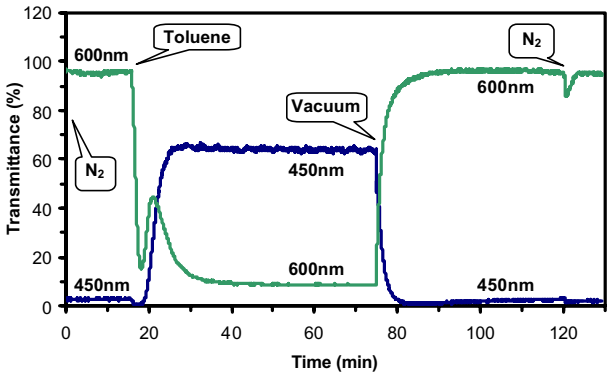

Figure 4 : Transmittance variation with time at 450 nm and 600 nm of the VOC sensor in presence of toluene (1000 ppm in dry nitrogen at 1 L/min)

The Figure 4 shows the transmittance variation with time at two different wavelengths (around an initial minimum at 450 nm and around an initial maximum at 600 nm) of a 600 µm thick birefringent porous glass fiber (same as presented in Figure 3) during intermittent contact with toluene vapors (1000 ppm in dry nitrogen flowing at 1 L/min). In the presence of toluene, the light intensity at 600 nm decreases rapidly down to ~15% of the initial intensity whereas at 450 nm, it increases rapidly from ~3% up to ~65% of the maximum intensity. The transition state kinetic may differ depending on the observation wavelength. For example at 600 nm the intensity initially drops rapidly due to the combined effects of birefringence diminution and transitory light diffusion. From about 2 to 5 minutes following toluene vapor initiation, the intensity increases as the diffusion transition state ends, then decreases down to a stationary state mainly due to a reduction in birefringence. At 450 nm, the intensity mainly increases up to a stationary level with almost no influence by transitory light diffusion since the initial transmission is close to zero.

Condensation of toluene into the porous structure is reversible and the solvent may be removed by a flow of pure nitrogen or more rapidly by vacuum as shown in Figure 4 (for time > 75 min) where the initial intensity values are recovered quite rapidly. The kinetics depends mainly on the applied vacuum.

DISCUSSION

The way a porous glass is produced strongly influences its final optical properties. For instance birefringence of porous glass produced from two-phase alkali borosilicate is dependent on the chemical composition, on the geometrical shape of the initial glass, on the phase separation process (including factors such as temperature, time of the heat treatment and mechanical strain by stretching or by compression), on the leaching process (including factors such as temperature, time, nature and concentration of the acids used for leaching as well as stirring conditions) and also on the post leaching treatments (including factors such as washing with water or dilute alkali solution and drying conditions) [3, 4, 6]. All of these multiple parameters may be used to tune the final birefringence of the porous glass as required or desired in order to adapt the performances of the sensor to specific industrial applications.

Interestingly in the presence of a chemical, capillary condensation could occur preferably where the curvature of the matrix wall is highest that is in the smallest pores first. But for a cylindrical pore with an oval cross-section, capillary condensation will also first tend to fill the high curvature surfaces creating a more circular cross-section before filling the pore, possibly reducing the contribution of the pore shape to the anisotropy [5].

Since capillary condensation could be also strongly influenced by the surface energy of the solid matrix which changes the surface tension of the condensed liquid, possible surface treatments of the porous glass could also be used for instance to make the porous glass hydrophobic and thus less sensitive to humid conditions.

One great advantage of this kind of optical sensor is its ability to react to a great variety of VOC since they usually have the capacity to condense into the micropores of the solid matrix. Using the experimental set-up described in this paper we tested successfully many other solvents than the one described here such as methanol (n_D 1.329, B_p 64.7°C), diethyl ether (n_D 1.353, B_p 34.6°C), acetone (n_D 1.359, B_p 56°C), ethyl acetate (n_D 1.372, B_p 77°C), 2-butanone (n_D 1.379, B_p 80°C), isopropyl alcohol (n_D 1.377, B_p 97°C), dichloromethane (n_D 1.424, B_p 40°C), cyclohexane (n_D 1.426, B_p 80.7°C) and styrene (n_D 1.54, B_p 146°C)… Such a broadband sensor could be used for instance for detecting VOC intrusion into a vehicular cabin or a building's air ducts in order to prompt switching a carbon filter into the air flow for purification purposes only when actually required, extending thus the life of such filter.

Another advantage of the technology presented here is its design flexibility. One can use a broadband light source such as halogen lamp and detect changes upon exposure to VOC in the transmitted light using a spectrometer as presented in this paper. Note that if the birefringence and the thickness of the porous glass are well selected, the phase shift induced during VOC detection could be strong enough to cause a color change so that human eye could be used as a light detector. In such case, proper additional color filters could be used to improve the detection contrast, or to help color blind people. Another possibility could be to use a narrow band light source such as laser or high intensity LED and a cheap broadband silicon based detector such as a photodiode. In such system light source and light detection could be fully controlled by a simple electronic conditioner that could warn the end user when a defined detection level has been reached.

Miniaturisation of the sensor

Simple miniaturized VOC sensors using the technology presented in this paper could thus be realized with cheap and robust materials such as LED light source, plastic or glass multimode optical fibers terminated by crossed polarizing films (such as Polaroid™), birefringent porous glass (which acts as sensing anisotropic material) and photodiode light detector. A schematic of such design is presented in Figure 5.

A small encapsulating perforated or permeable tube may conveniently be provided to maintain the various elements in proper orientation since the best contrast is obtained when the birefringent fiber is placed at 45° between the crossed polarizers. The optical fibers are used for light input to the birefringent porous glass and to collect to the light detector the output light signal. With such design, the miniature sensor could be placed in strategic remote locations minimizing also the flow disturbance.

It should be noted that commercially available Polaroid™ films generally do not efficiently polarize wavelengths above approximately 800 nm contrary to the Glan-Thompson polarizers used in this study (which have a wider range 350-2300 nm). However for most applications especially for those where human eye is used as a detector (color change) visible range is obviously suitable.

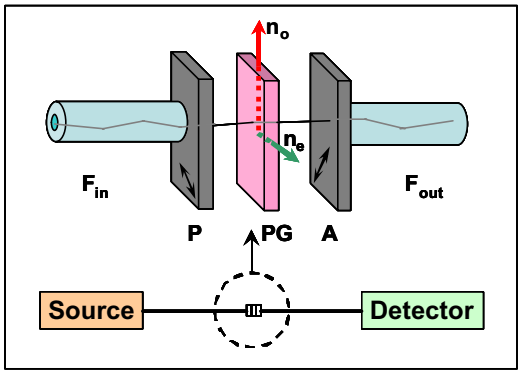

Figure 5 : Scheme of the miniaturized VOC sensor. Visible light is guided from the source to the detector using optical fibers (F_{in} and F_{out}) terminated by crossed polarizing films (P and A) facing the birefringent porous glass (PG)

At FISO Technologies we are presently working on developing a commercial product using this promising new technology in order to implement our variety of existing fiber optic sensors (visit us at www.fiso.com).

ACKNOWLEDGMENTS

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