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A Glass Slab Optical Waveguide Detector with an Optical Position Sensor for Flow Analysis

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An optical position sensor, which converts the shift of light beam center to voltage signal, was used to detect an analyte with a glass slab optical waveguide (SOWG) detector for flow analysis. The detector responded to mixtures of ethanol and water as well as methylene blue (MB) solutions, i.e., to change in the refractive index of the surface area of the SOWG. The detection limit of this system for MB solutions was half of that with the absorbance measurement using the SOWG.

Recently various kinds of planer optical waveguides have been applied to integrated opto-chemical 1,2 and -bio sensors, 3-5 in which the light absorption or the change of refractive index caused by analytes on the sensor surface is monitored. In the latter case, the change of the refractive index at a coupler of the waveguide, a grating coupler4 or a 'resonance mirror' type coupler5, affects the coupling efficiency between source light and the waveguide and/or the coupling conditions, e.g., the angle of the out-coupled light beam and so on; such changes have been utilized for chemical sensing. On the other hand, when a prism coupler, which is the simplest to use in chemical laboratories, is used in a waveguide chemical sensor, a sample solution does not usually touch with the coupler directly. Hence, the coupling conditions have not been presumed to change due to the kinds of the sample solution. Thus, the absorbance detection has mainly been applied to chemical sensing.^{1,2} We have also been applying a glass slab optical waveguide (SOWG) with a prism coupler to a visible absorption detector of flow analysis to detect trace amounts of several dyes and iron(II).6-8

In this paper, on the other hand, an optical position sensor, which converts the positional shift of light beam center to voltage signal, was applied to the glass SOWG detector with a prism coupler instead of the absorbance measurement. The sensor was found to respond to mixtures of water and ethanol as well as methylene blue (MB) solutions, i.e., to change in the refractive index of the surface area of the SOWG.

Potassium ion doped glass SOWGs were fabricated by an ionexchange process on commercial soda-lime slide glasses (S-1214 from Matsunami Glass Inc., Japan) in molten potassium nitrate at 673 K for 30 min to 2h.6 The SOWGs supported two modes of guided light. Figure 1 shows the schematic diagram of the measurement system. A He-Ne laser (632.8 nm, 2 mW, random polarization) was used for a light source. The SOWG was mounted on a 360° rotational stage with X-Y-Z translation. The laser light was coupled into the SOWG with a prism coupler (nD = 1.8785). The out-coupled beam was collected with a convex lens (focal length = 50 mm) to project a 1:1 image on an optical position sensor, i.e., a one-dimensional position sensing diode (PSD, 1x6 mm of sensing area, S3931 from Hamamatsu Photonics, Japan). Two polarizers were placed between the laser and SOWG and between the SOWG and PSD to select the polarization of propagating light. The current signal from the PSD was processed with an analog signal processing circuit C3683-01 (Hamamatsu Photonics); the voltage signals of the

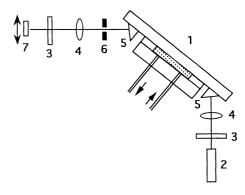


Figure 1. Schematic diagram of the present system. 1. SOWG flow cell, 2. He-Ne laser (633 nm), 3. polarizer, 4. convex lens, 5. prism coupler, 6. aperture, 7. PSD. Arrows shows the direction of the positional shift of light beam center.

positional shift of the light beam center (PSD response) and of the light beam intensity (absorbance signal) were simultaneously taken out from the circuit. Those signals were then amplified with digital voltmeters, and fed into a personal computer through a General Purpose Interface Bus (GP-IB). The flow cell on the SOWG was the same as that in the previous papers. Distilled water was used as a carrier and $0.5~\rm cm^3$ of a sample solution was introduced into the carrier stream via a loop injector. Mixtures of ethanol and distilled water and aqueous MB solutions ($5x10^{-6}$ to $10^{-4}~\rm mol~dm^{-3}$) were used as sample solutions.

Figure 2 shows the change of refractive index of the mixtures of ethanol and water and the PSD response to the mixtures. As shown in this figure, the PSD response corresponded to the change in the refractive index of the solution. The directions of the positional shift were opposite between TE₀ (TE: transverse electric) and TM₁, and TM₀ (TM: transverse magnetic). Moreover, the TM₀ mode gave the best sensitivity.

The present system was then applied to detect adsorbed MB molecules onto the SOWG surface, because the adsorption behavior of MB had been known from the previous work. 7 The adsorbed MB may cause the change in the refractive index of the SOWG surface as well as the light absorption.9 The PSD responded to the MB solution. In this case, the TE₀ mode gave higher sensitivity than the TM modes, although a TM mode usually give higher sensitivity than a corresponding TE mode in absorbance measurements with the SOWG.6,7 The reason for the difference in response is not clear at present. Moreover, the linear relationship between the PSD and the absorbance was observed up to 0.8×10^{-4} mole dm⁻³ of the MB solution (0.5 cm^3). Thus, the PSD response corresponds to the amounts of the adsorbed MB molecules. Then, the dependence of the PSD response upon the period of the ion-exchange process for the fabrication of the SOWG was investigated; the lowest detection limit for 0.5 cm³ of the MB solution (1.9x10⁻⁶ mole cm⁻³, S/N=2) was obtained with the SOWG prepared by 2 h ionexchange and was half of that with the absorbance detection.

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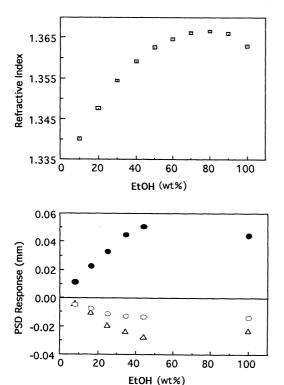


Figure 2. Dependence of refractive index on ethanol content (upper figure) and PSD response (lower figure).

•: TM_0 , $\circ: TM_1$, $a: TE_0$.

As described above, the PSD responds to the refractive index change of the surface area of the SOWG. However, the mechanism of the response may not be clear at present. The coupling conditions with the prism coupler, the angle of outcoupled beam etc., do not change due to the kinds of the sample solution. In other words, the PSD would not be presumed to respond to the kinds of the sample solution. As the PSD is known to show slight response to the change of the intensity of probe light beam, several experiments were done to eliminate such possibility in this work. Firstly, the PSD was placed transversely compared with the configuration in Figure 1; no response was obtained. Moreover, the optical configuration was changed to project a 1:2 image on the PSD. The sensitivity increased twice as high as that with the 1:1 image configuration, while the sensitivity of the absorbance detection remained unchanged. Thus, the PSD response is not due to the change of the light beam intensity, but due to the shift of the light beam center. Moreover, the wavelength of the light source was changed to 543 nm (a green He-Ne laser) in the MB measurements, and the results compared with those of 633 nm. The ratio of the absorbances (A₅₄₃ to A₆₃₃) was 0.4, while that of the PSD responses was 0.67. That is, the dependence of the signal

intensity upon the wavelength of the source light was different between the absorbance and PSD measurements. This result may also support that the PSD response is not due to the change of the light beam intensity. Tentatively, two mechanisms are under consideration. One is mode-mode interaction (TM₀-TM₁ and TE₀-TE₁) as proposed by Kuhn and Burgess in their work on the SOWG with a grating coupler.³ As a matter of fact, only the multi-mode SOWGs showed the PSD response in the present work. However, although the mode-mode interaction between TE_0 and TM_0 could be observed, that between TM_0 and TM_1 (or TE₀ and TE₁) would hardly be expected to occur according to the present waveguide theory. 10 The other is that the propagating light of each mode might originally have some distribution with the out-coupling angle; the change in the distribution of the light beam intensity within one mode causes the PSD response. Such distribution may occur due to relatively large heterogeneity in the refractive index of the guiding layer of the SOWGs used in this study. Although either mechanism can explain the observed PSD responses, we are still lacking in the experimental and theoretical bases to get conclusion.

Nevertheless, the present work can provide a sensitive detection method for not only a chromophore but also an analyte which causes the change in the refractive index of the surface area of the SOWG. Moreover, this is the first paper that describes a SOWG refractive index sensor in which a sample solution does not directly touch with a coupler. The present method can extend the applicability of the SOWG to chemical sensors in various fields.

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References and Notes

- M. D. Degrandpre, L.W. Burgess, P. L. White, and D. S. Goldman, *Anal. Chem.*, 62, 2012 (1990).
- S. S. Saavedra and W. M. Reichert, *Anal. Chem.*, 62, 2251 (1990).
- K. J. Kuhn and L. W. Burgess, Anal. Chem., 65, 1390 (1993).
- 4 P. M. Nellen and W. Lukosz, *Sens. Actuators, B*, **B 1**, 592 (1990).
- N. J. Goddard, D. Pollard-Knight, and C. H. Maule, Analyst, 119, 583 (1994).
- 6 K. Tsunoda, H. Itabashi, and H. Akaiwa, Bull. Chem. Soc. Jpn., 65, 1581 (1992).
- 7 K. Tsunoda, H. Itabashi, and H. Akaiwa, *Anal. Chim. Acta*, **276**, 133 (1993).
- 8 K. Tsunoda, H. Itabashi, and H. Akaiwa, *Anal. Chim. Acta*, **299**, 327 (1994).
- D. A. Higgins, S. K. Byerly, M. B. Abrams, and R. M. Corn, *J.Phys. Chem.*, 95, 6984 (1991).
- 10 H. Nishihara, M. Haruna, and T. Suhara, in "Optical Integrated Circuit," Ohm-sha, Tokyo (1985), pp. 51-65.