# A Slab Optical Waveguide with a Thin Glass Guiding Layer as an Absorption Detector in Flow Analysis

Kin-ichi Tsunoda,* Hiromitsu Itabashi, and Hideo Akaiwa
*Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376*

(Received July 6, 1995)

Developed was a slab optical waveguide (SOWG) in which thin sheet glass (20 to 200 μm thick) and a poly-tetrafluoroethylene-co-hexafluoropropylene film or air were used as a guiding layer and a clad, respectively. The sheet glass SOWG was evaluated as an absorption detector of flow analysis and gave higher sensitivity than a single-mode $K^+$ doped glass SOWG and comparative sensitivity with a radio frequency sputtered glass SOWG. Thus, this sheet glass SOWG can also be applied to flow analysis as a sensitive absorption detector.

A slab optical waveguide (SOWG) has recently been applied to an internal reflection element to perform highly sensitive spectroscopic measurements of thin films and surface phenomena in visible region.[1,2] The guiding layer of the SOWG is usually so thin (≤ several μm) that the number of internal reflection reaches to more than one hundred per cm, that resulting in a remarkable enhancement of the sensitivity. For such purpose, various types of SOWGs have been used, e.g., ion doped glass SOWGs,[3-6] glass or oxide SOWGs fabricated with sputtering methods,[7,8] and polymer SOWGs.[9] We have also been applying glass SOWGs to an absorption detector of flow analysis to detect trace amounts of several dyes and iron(II).[4-7]

On the other hand, although the use of thin sheet glass as an internal reflection element is rather classical, its potentiality has not been fully shown yet; sheet glass used in previous works was relatively thick, e.g., 150μm thick and more.[10,11]

In this paper, the SOWG which had a guiding layer of thinner sheet glass (down to 20 μm thick) was developed and applied to

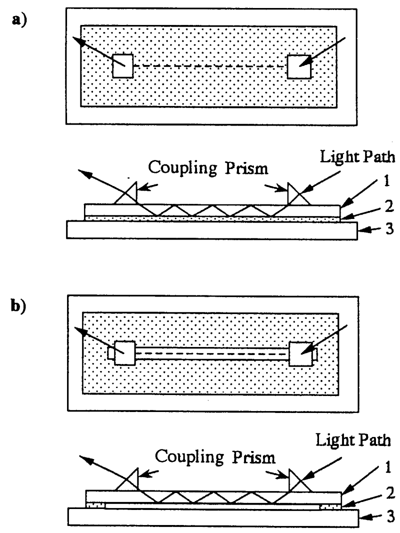


**Figure 1.** Schematic Diagrams of Sheet Glass Slab Optical Waveguides. 1. sheet glass (guiding layer), 2. FEP film, 3. slide glass. The clad is a FEP film in **a**), or air in **b**).

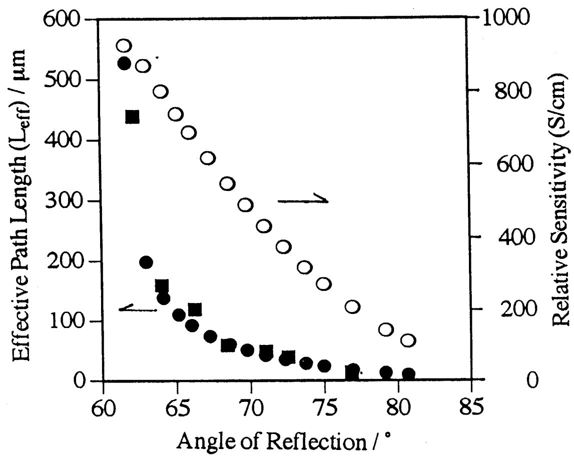


**Figure 2.** Dependence of $L_{eff}$ and S/cm on Angle of Reflection. Transverse electric (TE) mode. Guiding layer; BK7 (20 μm thick and $n_D$=1.517), clad; air ($n_D$=1.00), sample solution; water ($n_D$=1.333). ■ ; observed $L_{eff}$, ● ; calculated $L_{eff}$, ○ ; calculated S/cm.

an absorption detector of flow analysis, and was evaluated theoretically and experimentally in terms of effective path length ($L_{eff}$)[a] and relative sensitivity (S/cm).[b]

Figure 1 shows the schematic diagram of sheet glass SOWGs. Two types of SOWGs were made in this work. One is that the clad was a poly-tetrafluoroethylene-co-hexafluoropropylene (FEP) film (12.5 μm thick, $n_D$=1.338) (Figure 1a). The other is that the FEP film of the guiding area was removed as shown in Figure 1b, i.e., the clad was air. Three kinds of thin sheet glass were used as a guiding layer, i.e., 20μm thick (BK7, $n_D$=1.517, from Atock Co. Ltd., Japan) , 70μm and 200μm thick (Corning 0211, $n_D$=1.523, from Musashino Fine Glass Co. Ltd., Japan). Slide glass was used as a substrate. Special care was required to handle 20 μm thick sheet glass. However, reasonable durability was obtained, once the SOWG was assembled. The measurement system was the same as that of the previous paper.[4] A He-Ne laser (632.8 nm, 2 mW) was used as a light source.

*Experimental measurement of $L_{eff}$.* Solutions of the blue dye bromothymol blue (BTB, 0.25 to 5 mmol $dm^{-3}$, pH: 8.02) were used as absorbance standards to measure the $L_{eff}$ of the SOWG, because BTB molecules are not adsorbed on glass surface.[5]

*Theoretical calculation of $L_{eff}$ and S/cm.* The values of $L_{eff}$ and S/cm were calculated according to the references.[5,9,12] The step-wise distribution of refractive indices among a sample solution, a guiding layer and a clad (the step index SOWG) was postulated.

The S/cm for the step index SOWG (transverse electric (TE) mode as an example) has the following relationship with the thickness of a guiding layer (T) and the angle of reflection (θ) at the boundary of the sample solution and guiding layer.[5,12]

**Table 1.** Effective path length ($L_{eff}$) and relative sensitivity (S/cm) for various glass SOWGs

| SOWG | mode | $L_{eff}$/μm obs. | $L_{eff}$/μm calc.[a] | S/cm calc.[a] |
|---|---|---|---|---|
| Sheet Glass SOWG | | | | |
| 200μm, FEP clad | TE | 16 | 33 | 94 |
| 70μm, FEP clad | TE | 28 | 82 | 264 |
| 70μm, air clad | TE | 120 | 118 | 274 |
| 20μm, air clad | TE | 440 | 526 | 925 |
| $K^+$ doped SOWG[b] | $TE_0$ | 7 | 14 | 214 |
| RF sputtered SOWG[c] | $TE_4$ | 120 | 88 | 1200 |

a The maximum possible values.
b a single mode glass SOWG. Soda-lime slide glass was ion-exchanged in molten $KNO_3$ at 400 °C for 30 min.[5]
c unpublished data. A Corning 7059 glass target was sputtered for 10 h and the film was deposited on a quartz glass substrate. The guiding layer was ca. 5 μm.

$$S \propto \frac{\cos^2\theta}{T\sin\theta}$$

That is, larger θ and/or thinner T would give higher sensitivity. In the sheet glass SOWG, although the T value is larger than those of other types of glass SOWGs (≤ several μm), we can realize larger θ condition by using a lower refractive index clad such as a FEP film or air; that makes it possible to achieve the comparable sensitivity. Figure 2 shows the calculated $L_{eff}$, S/cm and observed $L_{eff}$ as functions of θ for the SOWG which has the 20 μm guiding layer and an air clad. Through SOWGs whose guiding layers are thinner (≤ several μm), only the lights of discrete θ values can be transmitted because of the boundary conditions. As for the sheet glass SOWG, on the other hand, the lights of continuous θ values larger than the critical angle ($\theta_c$) can be transmitted. As is seen from the figure, the values of those two parameters increase along with the decrease in the θ value down to the $\theta_c$ (61.49°). In particular, the values of $L_{eff}$ steeply increase when the θ value reaches to the $\theta_c$. Moreover, the observed $L_{eff}$s are in good agreement with the calculated ones. Table 1 summarizes the maximum observed $L_{eff}$ values and the maximum possible calculated $L_{eff}$ and S/cm values for various kinds of SOWGs fabricated by our group.[6] The present sheet glass SOWGs give much higher sensitivity than a single-mode $K^+$ doped glass SOWG, and comparative sensitivity with a radio frequency (RF) sputtered glass SOWG. In other words, this sheet glass SOWG would provide one oder of magnitude higher sensitivity than conventional spectrophtometry, if it were applied to flow analysis for Fe(II)-1,10-phenanthroline complex as described in the previous paper.[7] Thus, the sheet glass SOWGs can also be applied to flow analysis as a sensitive absorption detector. Although the SOWGs of FEP clad and of air clad should give almost the same $L_{eff}$ from the calculation, the air SOWG gave somewhat greater $L_{eff}$ than the FEP SOWG. As the attenuation of the guiding light was less in the air SOWG than in the FEP SOWG, particularly, in the region of the θ close to the $\theta_c$, the greater $L_{eff}$ was obtained with the air SOWG.

The sheet glass SOWG has some advantages over the other glass SOWGs. This SOWG is easy to fabricate and could be directly coupled with a source light without using a special type of coupler such as a prism or a grating coupler because of its thicker guiding layer, although the prism coupler was used in this work. Moreover, it could be applied to the absorption measurements in the UV region by using quartz sheet glass as a guiding layer. On the other hand, a possible drawback should be kept in mind, i.e., distortion in the absorption spectrum might occur, especially, if this was used at the θ value close to the $\theta_c$.[12]

This work was supported in part by a Grant-in-Aids for Scientific Research (No. 04554023) from the Ministry of Education, Science and Culture.

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$$A_{SOWG} = \varepsilon c L_{eff}.$$

Here, $A_{SOWG}$ is the absorbance obtained with the SOWG method, ε the molar absorption coefficient of an analyte, c the concentration of an analyte, and $L_{eff}$ the effective path length.[5,12] b) The relative sensitivity (S/cm) is the ratio of the sensitivity of the SOWG method (physical cell length 1 cm) to that of the conventional perpendicular irradiation method for adsorbed chromophore onto the SOWG surface. The S/cm and $L_{eff}$ have the following relationship;

$$L_{eff} = d_p S.$$

Here, $d_p$ is the penetration depth of evanescent wave from the SOWG surface into the sample solution.[3,5]