CHEMISTRY LETTERS, pp. 283-286, 1993.

Properties of Alkali-Ion-Exchanged Glass Optical Waveguides. Optical Sensitivity of Monitoring Chemical Species at Surface

Kiminori ITOH,* Masayuki MURABAYASHI, Kazuki YAMAZAKI,† and Akira FUJISHIMA†
Institute of Environmental Science and Technology,
Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240
†Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Glass optical waveguides (OWGs) doped with alkali ions were examined mainly in terms of optical sensitivity of monitoring surface chemical species located at surfaces. The maximum sensitivity (per 1 cm optical path length) for K^+-doped glass OWGs was ca. 50 times as large as that of conventional optical measurements with normal incidence of monitoring light. Rb^+-doped and Cs^+-doped OWGs had higher sensitivities, but they showed rather large attenuation of the guided light.

A typical optical waveguide (OWG) consists of a substrate and a thin top layer (waveguide layer) having refractive index larger than that of the substrate; a covering material (clad) is usually air. An interesting feature of this OWG is that the electric field associated with a lightwave propagating in the waveguide layer is very strong at the surface of the OWG; hence, very sensitive optical monitoring can be performed for chemical species located at the OWG surfaces on the basis of absorption and/or scattering of the guided light. For instance, we have carried out highly sensitive flash photolysis and spectroelectrochemistry using K^+-doped glass OWG.1)

Of many OWGs, alkali-ion-exchanged glass OWGs2) can be easily prepared, are convenient to use, and have good optical and mechanical qualities and relatively high sensitivity.1) There have been, however, no systematic studies on the optical sensitivity of the ion-exchanged glass OWGs so far. Thus, the present work aims to optimize experimentally and theoretically the sensitivity of the ion-exchanged OWGs. The K^+-doped OWGs were examined most extensively in this work although Rb^+ and Cs^+ ions also were tested as dopants. It was found that the sensitivity largely depends on the conditions of the ion-exchange process; these results were explained by solving the wave equations for the light propagating in the OWGs.

For ion-exchange, colorless crown glass slides (trade name "Shiro (white), polished", purchased from Matsunami Glass Co.) were immersed in a molten-salt bath for different periods of time in an electric furnace. The composition of the glass slides in molar fraction is as follows (according to the company): SiO_2 70%, Al_2O_3 1%, Na_2O 12%, K_2O 4%, CaO 6.5%, MgO 1%, BaO 1%, ZnO 4%, TiO_2 0.5%. The salts used were KNO_3, $RbNO_3$ and $CsNO_3$. The doped slides were cooled in air, and washed with water to remove the solid salt remaining on the OWG surfaces. These OWG samples were mounted on a stepping-motor-driven turntable, and angles of incidence for resonance coupling were measured by using a He–Ne laser (wavelength = 632.8 nm) for each propagation mode; glass prisms (*n* (refractive index) =1.75) were used as couplers to introduce the laser beam into the OWG layer.

To discuss the surface sensitivity of the OWGs, we introduce here sensitivity factor (*SF*) as a measure which represents as to how extensively the OWGs are sensitive compared to conventional optical measurements with normal incidence of monitoring light beams. *SF* values were experimentally estimated as follows, and were compared to theoretical values calculated below. First, methylene blue (MB) dye molecules were adsorbed onto the OWG surface from an aqueous solution, and optical density of the adsorbed dye (OD_{ad}) at 632.8 nm was measured in air using a UV–visible spectrophotometer. Second, *OD* values were obtained for guided TE (transverse eletcric) modes from attenuation of the guided light (OD_{OWG}). Finally, *SF* was estimated as OD_{OWG}/OD_{ad}. It should be noted that we used TE modes here because *SF* was estimated on the basis of the measurements with normal incidence of the monitoring light; that is, the electric field of the monitoring light is oscillating parallel to the OWG surface in these two cases. The value of *SF* thus obtained is proportional to optical path length of the portion of the OWG covered with the adsorbed dye molecules; therefore, *SF* per unit optical length was obtained by dividing the experimental *SF* values by the path lengh (3.3 cm in the present experiment).

Figure 1 shows the experimental *SF* values (symbols) for K^+–doped OWGs, plotted against ion-doping time (t_{dope}). The number m in the figure represents mode number, i.e., number of nodes that a standing lightwave in the waveguide layer has. The temperature of the melt (T_{bath}) employed was 400 °C, well above the melting point (339 °C). The highest *SF* (ca. 50/cm) was observed at ion–doping time between 0.5–1 h. This *SF* value is smaller than those for Sn–doped OWGs (float glass slides).[3] Attenuation of the guided light for K^+–doped OWGs was smaller than that for the Sn–doped OWGs.

The *SF* values obtained above were compared to theoretical ones based on the electric field distribution calculated by solving wave equations[5] numerically with the Runge–Kutta method. In this calculation, *n* of the surface of the OWG layer (n_f) was a parameter, and the average (n_{av}) of n_f and *n* of the clad (n_c=1.0, air clad) was employed as refractive index experienced by the surface species; i.e., $n_{av}=(n_c^2+n_f^2)^{1/2}$. By using these parameters, *SF* is expressed as follows:[1,7]

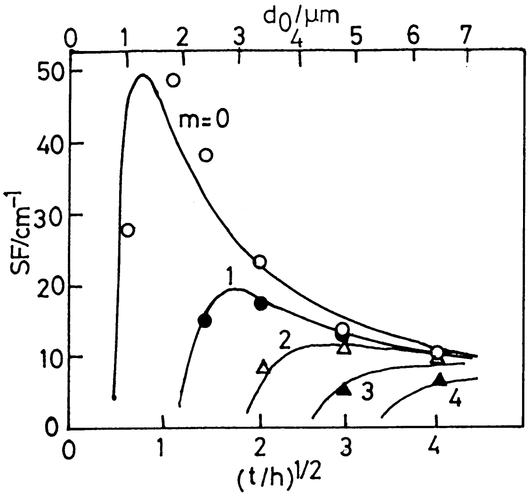

Fig. 1. Experimental *SF* (symbols in the figure) vs. immersion time (t), and theoretical *SF* (solid curves) vs doping depth (d_0).

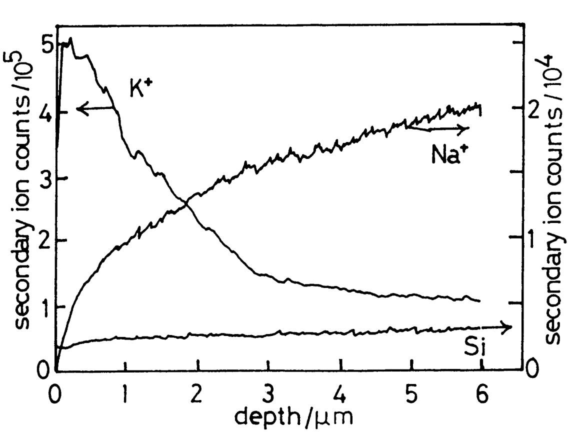

Fig. 2. Ion distribution of K^+, Na^+, and Si measured by SIMS.

$$SF = (n_{av}^2/2 \cdot N_{eff})E(0)^2/\int_{-\infty}^{+\infty} E(x)^2 dx \qquad (1)$$

Here, N_{eff} ($n_c < N_{eff} < n_f$, dimensionless value) is the effective refractive index of the guided mode in question obtained as an eigenvalue of the wave equation, and $E(x)$ is the electric field distribution obtained as the corresponding eigenfunction; x is the distance from the surface of the OWG. Thus, $E(0)$ is the electric field amplitude at the OWG surface; for instance, E(0) is of the order of 10^7 V/cm for a 1 mW light wave (633 nm) propagating in a OWG layer with 1 μm thickness. $E(x)$ has two components; i.e., one parallel to the surface, and the other normal to the surface. Our calculations are based on the former one because the TE modes were used as mentioned above.

To calculate *SF* using Eq. 1 we need $n(x)$, profile of n. Since *SF* depends largely on the shape of $n(x)$, we employed SIMS (secondary ion mass spectroscopy) to obtain a reasonably accurate ion distribution; although $n(x)$ is estimated often by using the inversed WKB method,[4)] it gives only a rough shape of $n(x)$. The ion distributions obtained experimentally with SIMS are shown in Fig. 2 for K^+, Na^+, and Si. The distribution of K^+ is close to a Gaussian function, and that of Na^+ close to upward exponential (when corrected by using Si as a standard). Thus, we used the two types of the distribution function for $n(x)$ to fit the experimental *SF* data. Theoretically-calculated *SF* values are shown in Fig. 1 by solid lines. In these calculations, we used the Gaussian distribution (i.e., $n(x) \propto \exp\{-(x/d_0)^2\}$), and assumed that the diffusion depth, d_0, is linear to $(t_{dope})^{1/2}$; other parameters used are n_f = 1.5195, n_s = 1.51 (refactive index of the glass substrate), and n_c = 1.0. The curves fit the observed *SF* values well while exponential functions gave poor fittings (not shown in the figure). Thus, $n(x)$ can be approximated by the Gaussian distribution; this result is consistent with the conclusion of Ref. 9.

Next, we discuss effect of T_{bath} on *SF*. Figure 3 shows that *SF* took the highest value for T_{bath} of 400 °C when immersion time was 1 h. This result suggests that this immersion time was close to the optimum condition for T_{bath} = 400 °C. However, main reason for the large decrease in *SF* for the higher temperatures is likely that n_f decreases as T_{bath} increases, and thereby *SF* decreases. This can be seen in Figs. 4 and 5. Figure 4 compares n profiles for different T_{bath}s; the inverse WKB method[4)] was used to convert the experimental N_{eff} values to n profiles. Small n_f results in small *SF* as Fig. 5 shows; in this calculation, effective thickness of the OWG layer (= d_0) was changed to give the optimum *SF* for each n_f. Thus, high T_{bath}s caused to decrease *SF*. Furthermore, too high T_{bath}s cause corrosion of the glass substrates. In conclusion, lower T_{bath}s are favorable to get high *SF* values as long as the ion-exchange process is easily performed; T_{bath} = 400 °C is reasonable in this respect, because *SF* is nearly the highest and the KNO_3 melt is not too viscous to immerse glass slides quickly.

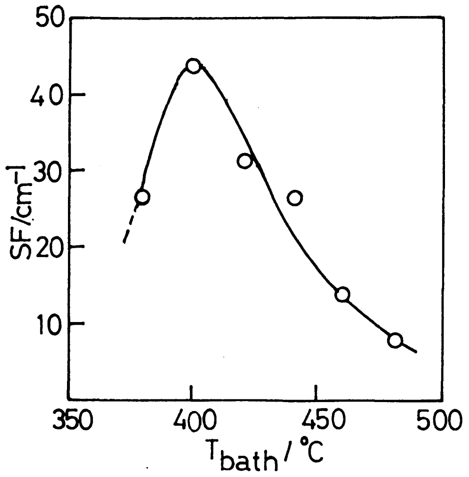

Fig. 3. *SF* vs. molten-salt temperature; immersion time = 1 h.

The corrosion of the substrates was significant in the $CsNO_3$ baths. In fact, it was difficult to obtain the

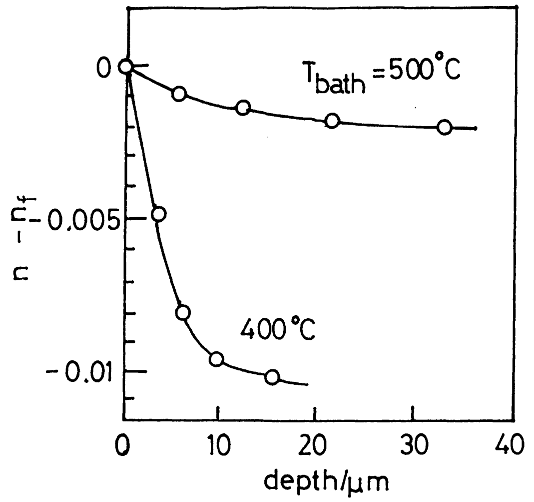

Fig. 4. Refractive index profiles calculated by using the inverse WKB method for different molten-salt temperatures.

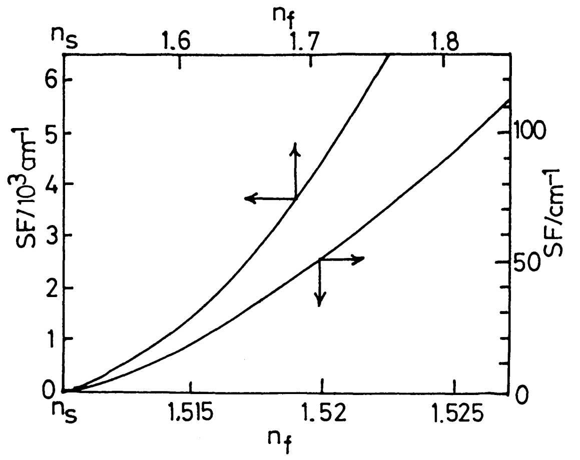

Fig. 5. Calculated *SF* values vs. refractive index of the waveguiding layer.

optimum *SF* for Cs^+ because scattering of the guided light was significant owing to roughened OWG surfaces although *SF* of the Cs^+-doped OWGs were 200/cm at least. For Rb^+, *SF* was about twice that for K^+, but attenuation of the guided light was still much larger than the K^+-doped OWGs.

Although this work discussed limited combinations of glass substrates and ions, general aspects of ion-exchanged glass OWGs for surface monitoring were made clear. That is, the surface sensitivity can be controlled by changing dopant ions, doping temperature, and doping time. Moreover, we can estimate the surface sensitivity on the basis of numerical solutions of the wave equations; SIMS (for ion distributions) and the inverse WKB method (for the estimation of refractive-index changes) are of great help.

This work was supported in part by Nihon Sheet Glass Foundation for Materials Science, Iketani Science and Technology Foundation, and Tokyo Ohka Foundation. The authors thank to Dr. O. Odawara of Tokyo Institute of Technology for his kind measurements of the ion distributions using SIMS.

References

1) K. Itoh and M. Murabayashi, "Trends in Physical Chemistry," ed by Council of Scientific Research Integration, Research Trends, India (1991), p. 179, and references therein.
2) R. V. Ramaswamy and R. F. Srivastava, *J. Lightwave Technol.*, **6**, 984 (1988), and references therein.
4) J. M. White and P. F. Heidrich, *Appl. Opt.*, **15**, 151 (1976).
3) K. Itoh, H. Niikura, O. Odawara, and M. Murabayashi, *Jpn. J. Appl. Phys.*, **30**, 3416 (1991).
5) For instance, H. Nishihara, M. Haruna, and T. Suhara, "Hikari Shuseki Kairo (Integrated Optics)," Ohm Sha, Tokyo (1985), Chap. 2.
6) J. D. Swalen, M. Tacke, R. Santo, K. E. Rieckhoff, and J. Fischer, *Helv. Chim. Acta.*, **61**, 960 (1978).
7) J. Albert and G. L. Yip, *Appl. Opt.*, **24**, 3692 (1985).

(Received November 10, 1992)