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Ion-Exchanged Glass Optical Waveguide Systems for Surface Spectroscopy. Composite Structures for Realization of High Sensitivity and Low Loss

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A K^+-doped glass optical waveguide (OWG) and an Ag^+-doped glass OWG were combined on one substrate using tapered velocity couplers to realize OWG systems for surface spectroscopy with high sensitivity and low loss. The high sensitivity part (Ag^+-doped region) was more than 1000 times sensitive compared with optical measurements with normal incidence of monitoring light.

The optical waveguide (OWG) method is useful for surface spectroscopy, i.e., monitoring surface molecules and their reaction dynamics. For instance, photocatalytic reactions and electrochemical reactions have been sensitively monitored.[1-3] Moreover, sensitive chemical sensors have been fabricated using OWG techniques.[4,5] Glass OWGs doped with K^+ ion[1-3,5] often employed in these studies are convenient OWGs with little loss of guided light, but they have relatively low sensitivities. Their relative sensitivities, S_{OWG}, were 50-100/cm; that is, they were 50-100 times sensitive (per cm optical path) compared with optical measurements with normal incidence of light. Thin films deposited onto transparent substrates exhibit very high sensitivity, but they usually show large loss of guided light mainly because of surface roughness. Absorption sometimes causes high attenuation even when absorption coefficient of the film is small.[6] Thus, high sensitivity and low loss seem to be contradictory properties of OWGs when applied to surface spectroscopy. An approach we have proposed to overcome this difficulty is to construct composite structures which have a low loss part and a high sensitivity part separately on one substrate (cf. Fig. 1); the low loss part has small refractive index (n_{OWG}), e.g., K^+-doped glass OWGs (n_{OWG}=1.515-1.518), and the highly sensitive part has large n_{OWG}. We recently have built this type of OWGs composed of a K^+-doped OWG and a $FePO_4$ thin film (n_{OWG}=1.72); S_{OWG} > 5000 was achieved, and the OWG proved effective for monitoring internal structures of the thin film; however, the loss at the sesitive part was too large (>20 dB/cm)[7,8] for general surface monitoring. Thus, it is still necessary to develop effective composite systems using other materials; in particular, we should survey suitable materials for the high sensitivity part. In this paper, we employed Ag^+-ion doping (maximum n_{OWG} = 1.6[9]) for the high sensitivity part, and K^+-doping for the low loss part; moreover, mixed molten salts were used to control Ag^+ ion concentration which largely affects the magnitude of the loss of guided light. Thus, reasonably high sensitivity and low loss were achieved.

Figure 1 shows the structures of the composite OWGs and principle of their operation; the type A OWG was described in this paper. The OWGs were prepared in the following manner. First, the thick

OWG part (K^+-doped layer) was made by immersing substrate glass into KNO_3 melt at 400 °C for 30 min; thickness of this layer was around 1 μm. The substrates used were microscope glass slides made of crown glass, "Shiro Fuchimigaki (white edge-polished)" purchased from Matsunami Glass Co., Ltd. Second, a piece of glass plate (1 cm wide) covered with melt containing $AgNO_3$ was placed on the K^+-doped OWG, and the whole sample was heated in an electric furnace at 300 °C for different periods of time. We note here that no further diffusion of K^+ occurs at 300 °C. Thus, a part of the OWG was doped with Ag^+ ion to have high sensitivity, and inevitably, large loss. The monitoring light was introduced into or out of the OWG from a prism or a single-mode optical fiber attached to the K^+-doped part, and the guided light can avoid excess attenuation due to large loss in the sensitive part.

To transfer the guided light from the K^+-doped part to the Ag^+-doped part (and vice versa) as the arrows show in Figure 1, adiabatic transition should take place as Figure 2 schematically demonstrates. In Figure 2, effective refractive index (N_{eff}) was plotted against thickness of the Ag^+-doped part; T=0 corresponds to the K^+-doped part where no Ag^+-doping was applied. The value of N_{eff} continuously changes from that in the K^+-doped part (N_{eff}=1.515) to that in the Ag^+-doped part (N_{eff} > 1.52) when the transition takes place slowly enough; slopes with length of 0.5–1 mm are required for this adiabatic transition.[7] On the contrary, the guided light remains mainly in the K^+-doped layer (beneath the Ag^+-doped layer in Figure 1A) when the slope is too short. Thus, the length of the transition part (called taper velocity coupler[7]) is very important in this OWG system. We examined cross section of our OWG samples with an electron-probe micro analyzer (EPMA); it was found that the thickness of the Ag^+-doped part gradually changed along the surface of the OWG, and the slope was sufficiently long.

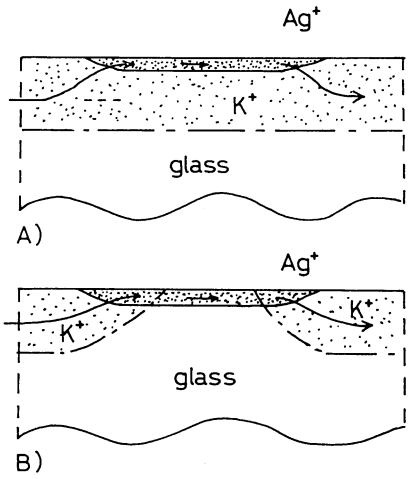

Fig.1. Structures of the composite OWGs and principle of their operation. The arrows show how the guided light is transferred from one part of the OWG to another part via adiabatic transition.

Relative sensitivity (S_{OWG}) of the composite OWGs was estimated on the basis of optical absorption of dye molecules adsorbed onto the OWG surfaces. The monitoring light source used was a He-Ne laser with multi-wavelengths. The dyes employed were rhodamine B for monitoring at 543.5 nm, and methylene blue for 632.8 nm; concentration of aqueous solutions of these dyes were 10^{-4}–10^{-5} mol/dm^3. Glass prisms with high refractive index (n=1.75), and a matching liquid (methyleneiodide, n=1.75) were used to couple the laser beam with the OWG. Solution reservoirs with width of 2–5 mm were employed because small optical paths were necessary for highly sensitive OWGs to conduct accurate measurements of S_{OWG}. Optical absorption of the adsorbed

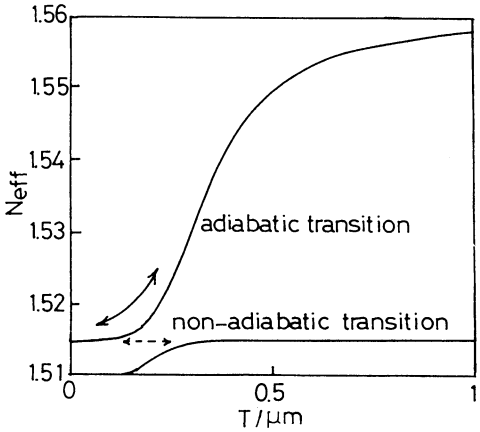

Fig.2. Adiabatic and nonadiabatic transition of the guided light on calculated dispersion curves. T is width of the Ag^+ distribution, and N_{eff} is effective refractive index of the composite system.

dye was measured on the OWGs and with a spectro-photometer after the filter paper was removed; TE mode was employed in the present OWG experiments considering that transition moment of the dyes used is parallel to the solid surfaces to which the dyes are adsorbed.[10]

S_{OWG} and the loss of guided light were largely dependent on $AgNO_3$ concentration ([$AgNO_3$]) in the molten salt bath. As a matter of fact, the loss observed for OWGs prepared in pure $AgNO_3$ baths were so large that no mode was detected; this large loss can be interpreted in terms of formation of colloidal Ag.[9] Thus, mixed molten salts of $AgNO_3$, KNO_3, and $NaNO_3$ ([KNO_3]:[$NaNO_3$]=1:3) were used to control Ag^+ ion concentration. The loss was not too large for [$AgNO_3$]<10%, and hence, [$AgNO_3$] = 5% was employed in the experiments below.

Figure 3 shows detailed measurements (symbols in the figure) and analyses (solid and dashed curves) of S_{OWG}; the abscissa ($t_{bath}^{1/2}$)is square root of the time of ion-exchange in the $AgNO_3$ bath . The maximum S_{OWG} observed was ca. 1400/cm for 543.5 nm, and ca. 1300/cm for 632.8 nm; these values are 20-30 times as large as those observed for K^+-doped OWGs,[10] and are little less than that calculated with n_{OWG}=1.6, that is, maximum value for Ag^+ doping. Thus, it proved that even [$AgNO_3$]=5% gave sufficiently high Ag^+ concentration in the OWG layer although time of doping tended to increase compared to pure $AgNO_3$ baths. The loss of guided light increased with S_{OWG}, and was ca. 5 dB/cm at the maximum S_{OWG}; the loss, however, further increased for longer doping times while S_{OWG} decreased.

The curves in Figure 3 are theoretical values of S_{OWG} based on numerical calculation (Runge-Kutta method) and a simple model. In this calculation, refractive index distribution in the OWG layer, $n(x)$, was represented by a summation of contributions from Ag^+ ions and K^+ ions, and Gaussian distribution was assumed for both ions; this has been confirmed using secondary ion mass spectroscopy (SIMS) for K^+,[10] and is first approximation for Ag^+. Thus, $n(x) = n_s + \Delta n_{Ag+} \exp(-(x/T_{eff,Ag+})^2) + \Delta n_{K+} \exp(-$

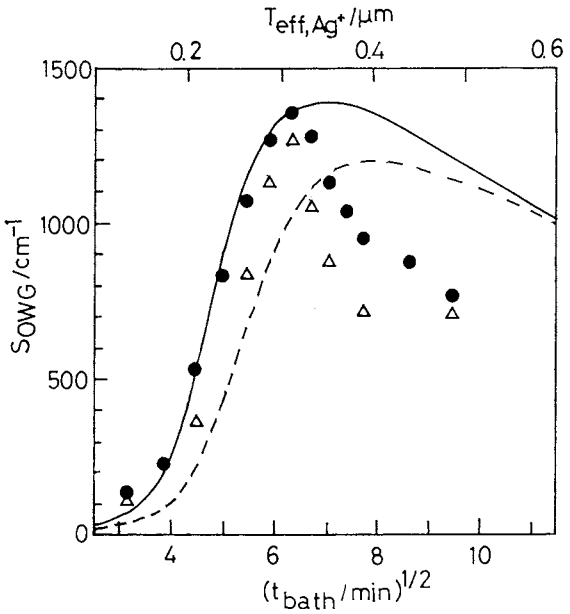

Fig.3. Experimental and calculated sensitivities (S_{OWG}) of the composite OWGs. Experimental values: o (at 545 nm) and Δ (at 633 nm). Calculated values: solid line (for 545 nm) and dashed line (for 633 nm).

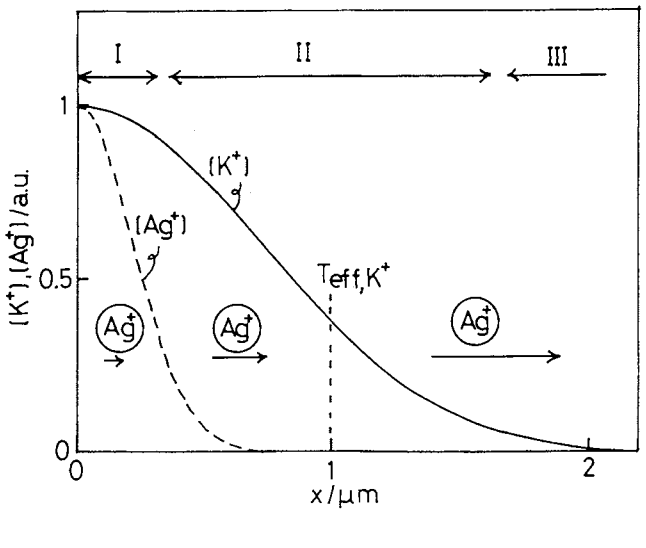

Fig.4. Diffusion rate of Ag^+ ions changes depending on K^+ concentration in the OWG layer. Region I, high [K^+]: region II, medium [K^+]: region III, low [K^+]. The dashed curve is [Ag^+] for maximum S_{OWG}.

$(x/T_{eff,K+})^2$), where x is the distance from the surface to the bulk, n_s is n of the glass substrate (=1.51), Δn_{Ag+} and Δn_{K+} denote refractive index changes induced by these ions, and $T_{eff,Ag+}$ and $T_{eff,K+}$ are effective thicknesses of the distribution of each ion species. Of these parameters, $T_{eff,K+}$ was set to be 1 μm and Δn_{K+}=0.008. $T_{eff,Ag+}$ was assumed to be linear to $(t_{bath})^{1/2}$; this approach was sufficiently successful for K^+-doped OWGs.[10] $T_{eff,Ag+}/t_{bath}^{1/2}$ and Δn_{Ag+} were adjustable parameters. The curve fitting process was carried out in such a manner that the calculated curve coincided well with the rising part of the S_{OWG} observed for 543.5 nm; this appeared most successful among several fitting procedures tested. The final values of the fitting parameters were Δn_{Ag+}=0.08 and $T_{eff,Ag+}/t_{bath}^{1/2}$=0.52; the former value gives n_{OWG}=1.598, which is close to its possible maximum value of 1.6, and the latter gave reasonable $T_{eff,Ag+}$ values. The calculation also agreed with the experimental results with respect to the observation that S_{OWG} values for 545 nm are larger than those for 632.8 nm.

The fitting was unsuccessful for large t_{bath} values. This discrepancy can be explained by taking account of diffusion processes of Ag^+ ions in inuniformly distributed K^+ ions as Figure 4 schematically shows. We consider here that diffusion rate of Ag^+ decreases as K^+ concentration increases; this is based on our observation that longer ion exchange time was required for K^+ doped OWGs than for glass slides applied no K^+ doping. When considered the Gaussian distribution of K^+, K^+ concentration can be regarded to be nearly constant in region I in Figure 4, and hence, we can assume nearly constant diffusion coefficient (and constant $T_{eff,Ag+}/t_{bath}^{1/2}$ ratio) in this region. Thus, the curve fitting in Figure 3 is rationalized for short t_{bath} regions; however, the $T_{eff}/t_{bath}^{1/2}$ ratio should be increased for Ag^+ ions diffusing in regions II and III where K^+ concentration is decreased with x, and thickness of the OWG layer, $T_{eff,Ag+}$, becomes much larger than that calculated using the constant $T_{eff,Ag+}/t_{bath}^{1/2}$ ratio for initial diffusion. Another OWG structure depicted in Figure 1 (type B) has no such problem although its preparation is relatively complicated, and moreover, appeared to have larger losses. We are now testing as to which OWG structure is advantageous for the purpose of surface monitoring.

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