# Highly Sensitive and Low Loss Ion-Exchanged Glass Optical Waveguides Constructed by the Successive Doping of $K^+$ and $Ag^+$ Ions

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A $K^+$ ion-exchanged glass optical waveguide (OWG) was combined with an $Ag^+$ ion-exchanged glass OWG on one substrate by tapered velocity coupling to obtain a low loss and highly sensitive ion-exchanged OWG system. The relative sensitivity of the $Ag^+$-doped region was more than 1000 times per unit length (the reference here being spectroscopic measurements with normal incidence of monitoring light). The attenuation of the guided light was 3—5 $\mathrm{dB\,cm^{-1}}$ at the highly sensitive part. Stability against heat and against UV-irradiation were investigated also.

Optical waveguides (OWGs) have been used in fabricating optical devices in many areas. In particular, several kinds of OWGs have been applied to surface spectroscopy on the basis of a strong electric field at the OWG surface associated with a lightwave propagating in the waveguide layer.[1—4] For instance, simple one layer OWGs were used to monitor photocatalytic reaction of particulate $TiO_2$ adsorbed onto glass OWGs;[2,3] and two layer OWGs were constructed for spectroelectrochemical use and for Raman spectroscopy.[4,5,9] In the OWG spectroscopy, it is important to use, or develop, particular types of OWGs for particular spectroscopic measurements.

In this research, we aimed to develop low cost OWGs with high surface sensitivity for surface spectroscopy. This type of OWGs is suitable for OWG based bio- and chemical sensors. Of many kinds of optical waveguides, ion-exchanged glass OWGs can be easily prepared and their good optical and mechanical qualities at low cost are attractive. Among the ion-exchanged glass OWGs, the $K^+$-doped glass OWG is known to show low loss (<0.5 $\mathrm{dB\,cm^{-1}}$), and in fact, has been used in the former work,[1—4] and also studies of sensitive chemical sensor,[6,7] although its sensitivity is relatively low.

In previous papers, we have pointed out that high sensitivity can be obtained with thin OWGs made of materials having high refractive index.[1—3] These OWGs, however, tend to have large propagation losses. Thus, the high sensitivity and low loss seem to be contradictory with each other. An effective idea to overcome this difficulty is the use of composite OWGs based on tapered velocity couplers as we have already shown using $FePO_4$ thin film OWGs coated onto $K^+$-doped OWGs; however, losses due to the thin film OWG were still high in this system.[7,9]

In this paper, we presented a new composite OWG system constructed only from ion-exchanged OWGs, and demonstrated that they have sufficiently high sensitivity and reasonably low loss. In addition, the stabilities of the OWG against heat and UV-irradiation were investigated to examine their weatherability.

## Theoretical

**Design of the Composite OWGs.** At first, we discuss "relative sensitivity" of the OWGs, $S_{\mathrm{OWG}}$, which expresses how sensitive the OWG is compared with conventional optical measurements based on monitoring light normally incident to the sample surface. Since experimental evaluation of $S_{\mathrm{OWG}}$ is described later, we give here theoretical considerations. $S_{\mathrm{OWG}}$ for two-dimensional optical waveguides can theoretically be expressed as Eq. 1.[10]

$$S_{\mathrm{rel}} = (n_{\mathrm{surf}}^2/2N_{\mathrm{eff}})E_{\mathrm{y}}(0)^2 \Big/ \int_{-\infty}^{+\infty} E_{\mathrm{y}}(x)^2\mathrm{d}x \qquad (1)$$

Here, $n_{\mathrm{surf}}$ is the average surface refractive index and $N_{\mathrm{eff}}$ is the effective refractive index of the waveguide. From Eq. 1, we see that a big change of surface refractive index ($\Delta n$) induced by ion-exchange causes a high sensitivity of OWG ($S_{\mathrm{OWG}}$).[1] For the $K^+$-doped OWGs, the surface index change is 0.002—0.01, and the sensitivity, $S_{\mathrm{OWG}}$, is at most only 50—100 times per centimeter of optical path. On the other hand, the surface index change of $Ag^+$-doped glass OWGs is 0.01—0.09, and the maximum relative sensitivity, $S_{\mathrm{OWG}}$ is about 1500 times/cm according to theoretical calculations; its attenuation, however, is much larger, about

4—15 $\mathrm{dB\,cm^{-1}}$ mainly because of the surface roughness generated during the ion-exchange process.[11] Thus, the $Ag^+$-doped glass OWG is difficult to use as it is. With the idea we reported in the previous papers,[8,9] we constructed new type OWGs to overcome this difficulty; two types of composite glass OWGs were designed by combining the $K^+$-doped glass OWG with $Ag^+$-doped one on one glass substrate, as shown in Fig. 1. To transfer the guided light between the $K^+$-doped part and the $Ag^+$-doped part, as the arrows show in Fig. 1, adiabatic transition should take place as Fig. 2 schematically demonstrates; and a sufficiently long slope (0.5—1 mm) connecting two OWG layers is necessary for its operation.[8]

## Experimental

**Preparation of the Composite Ion-Exchanged OWGs.** Microscope glass slides (76×26 mm) made of crown glass, "Shiro Fuchimigaki (white edge-polished)" purchased from Matsunami Glass Co., Ltd., were used as substrates. The preparation of the OWGs was carried out in the following way. First, a preheated glass substrate was dipped into $KNO_3$ melt at 400 °C for 30 min to obtain a $K^+$-doped OWG layer, the thickness of which was about 1 µm. Second, a piece of frosted glass (10×26 mm) covered with a thin layer of $AgNO_3$ mixed with $KNO_3$ and $NaNO_3$ was fixed onto the $K^+$-doped OWG with a clamp, and the whole sample was heated at 300 °C in an electric furnace for 5—90 minutes. The $Ag^+$ ion-exchange takes place on the surface of $K^+$-doped OWG, but there occurs no further diffusion of $K^+$ at this temperature. Thus, type A in Fig. 1 composite ion-exchanged glass OWGs were obtained. In this experiment, a series of mixed molten salts of $AgNO_3$, $KNO_3$, and $NaNO_3$ ($[KNO_3]:[NaNO_3]=1:3$) were tested; the concentration of $AgNO_3$ was 0.1—50 mol%.

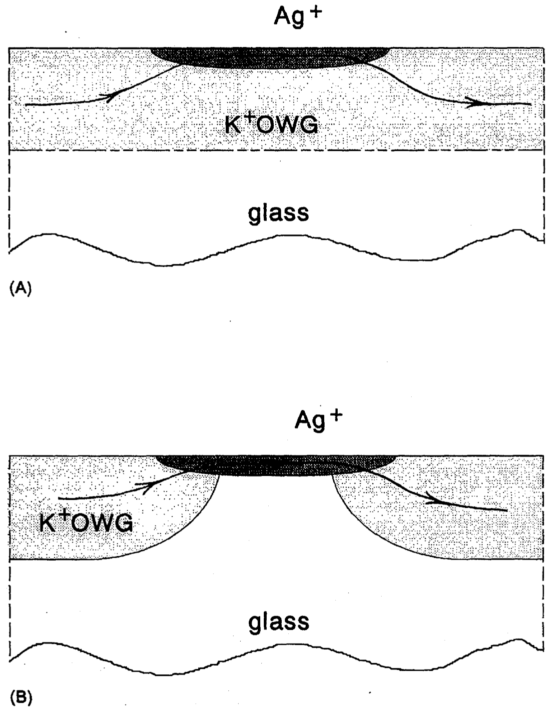

Fig. 1. Structures of the composite OWGs and the principle of their operation. The arrows show how the guided light is transferred from one part of the OWG to another part via adiabatic transition.

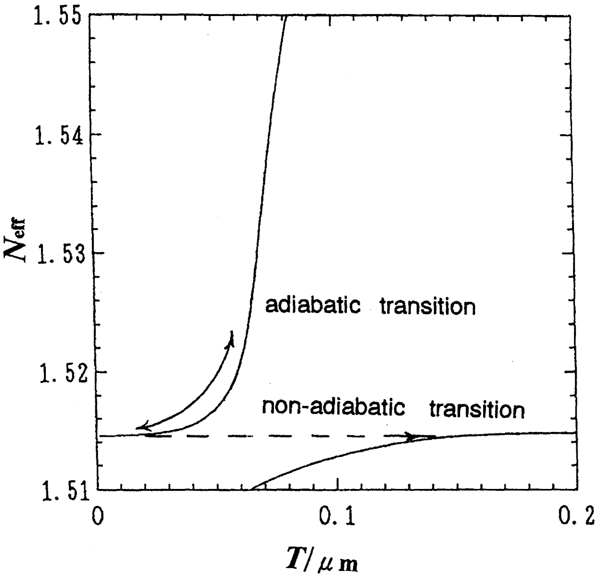

Fig. 2. Adiabatic and nonadiabatic transition of the guided light on calculated dispersion curves. $T$ is width of the $Ag^+$ distribution, and $N_{\mathrm{eff}}$ is effective refractive index of the composite system.

**Properties of the Composite Ion-Exchanged OWGs. Measurement of the Surface Relative Sensitivity:** The relative sensitivity of the composite ion-exchanged OWGs was appraised with a dye molecular absorption method.[10] A multi-wavelength He–Ne laser was used as a monitoring light source. The dyes employed were Rhodamine B for the monitoring at 543.5 nm, and Methylene blue for 632.8 nm; the concentrations of aqueous solution of these dyes were $10^{-4}$—$10^{-5}$ $\mathrm{mol\,dm^{-3}}$. Glass prisms with high refractive index ($n=1.75$), and a matching liquid (diiodomethane, $n=1.74$) were used to couple the laser beam into and out of the OWGs. A piece of filter paper of 2—5 mm width was used as a solution container because small optical paths were necessary for highly sensitive OWGs to gain accurate values of relative sensitivity. Using the apparatus shown in Fig. 3, the intensity change ($I_0 \rightarrow I$) of the monitoring light was measured with a photomultiplier after the dye was adsorbed onto the OWG, and $\Delta OD_{\mathrm{OWG}}$ was calculated as $\log(I_0/I)$. Next, $\Delta OD_{\mathrm{ABS}}$ of the dye absorbed on the OWGs was obtained with a spectrophotometer. Relative sensitivity, $S_{\mathrm{OWG}}$, can be obtained with the ratio, $(\Delta OD_{\mathrm{OWG}}/\Delta OD_{\mathrm{ABS}})/L$($L$ being the width (cm) of the region covered with the absorbed dye). We mention here that TE modes (TE0 in particular) were employed in this method because transition moments of the dyes used are parallel to the OWG surface when the dyes are adsorbed onto it.[1]

**Attenuation at the Composite OWGs:** The moving prism method was used to measure the attenuation of the guided light in the composite OWGs as shown in Fig. 4. The inlet prism was fixed on position C, then the outlet prism was moved from A to B, and the intensity of the monitoring light from the outlet prism on positions A ($I_A$) and B ($I_B$)

was measured. The attenuation ($\alpha$) of the $Ag^+$-doped region was obtained by calculating with the Eq. 2 below;[13] here, $L_{AB}$ is the distance from position A to B.

$$\alpha = |10 \times \log(I_B/I_A)/L_{AB}| \ (\mathrm{dB\,cm^{-1}}) \qquad (2)$$

**Annealing Property:** Annealing was carried out in an electric furnace at 400 °C for 2.5—10 min. The relative sensitivities of the composite OWGs were measured before and after the annealing.

**Effect of UV-Irradiation:** The composite OWGs were irradiated with 254 nm UV-light, and the intensity change of the monitoring light was measured. The distance between the UV-light source and the OWG sample was 10 cm.

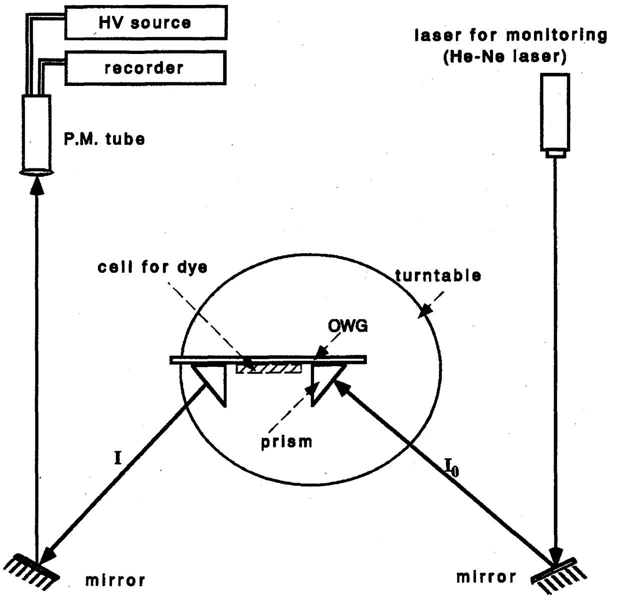

Fig. 3. The apparatus used for sensitivity testing.

## Results and Discussion

**Propagation of the Monitoring Light in the Composite OWGs.** Figure 5 shows how the monitoring light propagates in the composite OWG. The bright line corresponds to the region of the $Ag^+$-doped OWG and shows light scattering due to surface roughness. On the contrary, at the low loss areas of the $K^+$-doped OWG, no trace of the light scattering was observed. This shows that the guided light was successfully transferred from the $K^+$-doped layer to the $Ag^+$-doped layer and vice versa. The cross section of the composite OWG was examined with an electron-probe micro analyzer (EPMA) and the result is shown in Fig. 6. The thickness of the $Ag^+$-doped part grad-

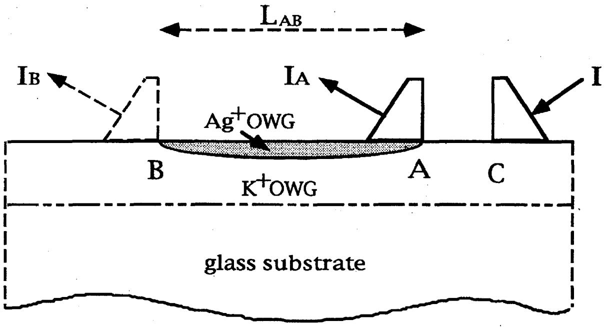

Fig. 4. Moving prism method used for attenuation measurements. The inlet prism was fixed on C, and the outlet prism was moved from A to B; $L_{AB}$ is the distance of the two prism positions.

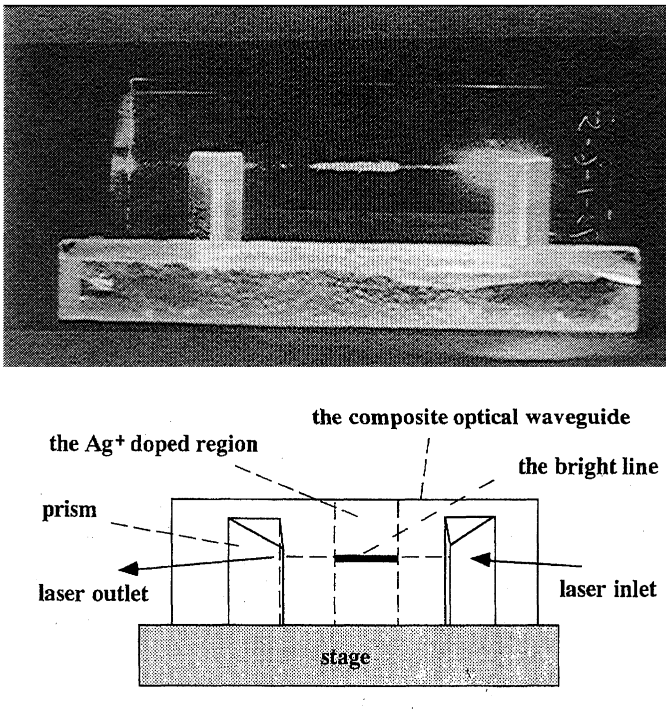

Fig. 5. Propagation of the guided light in the composite OWG. The bright line is observed at the $Ag^+$ doped region, and no distinct line at the $K^+$ doped region.

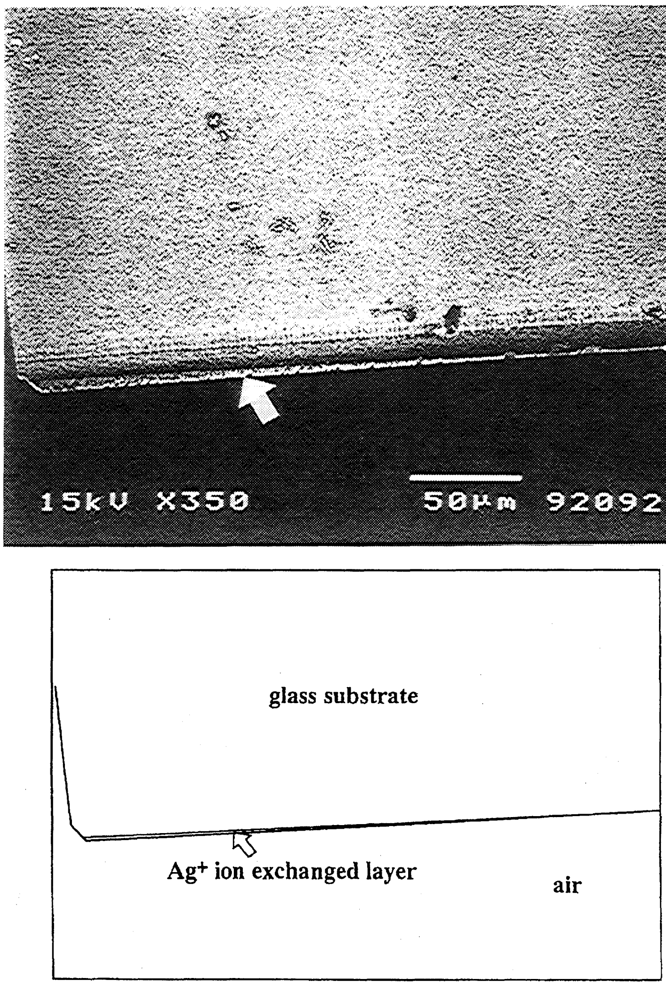

Fig. 6. The cross section of the composite OWG, observed with EPMA. A slowly changing slope of the $Ag^+$ doped layer can be observed as shown by an arrow.

ually changed along the OWG surface, and the slope was several hundred µm long, long enough for adiabatic transition to occur in this case.

**Sensitivity and Attenuation of the $Ag^+$-Doped OWGs.** It is obvious that the sensitivity and attenuation of the composite OWGs are determined mainly by the $Ag^+$-doped region because of the high sensitivity and the large loss of the $Ag^+$ ion-exchanged OWG. Both characteristics largely depend on the $AgNO_3$ concentration ($[AgNO_3]$) in the molten salt bath. As a matter of fact, the loss observed for the OWGs prepared in pure $AgNO_3$ baths was so large that no mode was obtained; this large loss can be interpreted in terms of formation of colloidal Ag on the surface of the OWG.[14] Thus, $KNO_3$ and $NaNO_3$ were used to control $Ag^+$ ion concentration. The ratio $[K^+]/[Na^+]$ in the mixed molten salts was set to be 1/3, which is the same as that in the glass substrate, so that no further $K^+$ ion-exchange occurs during the $Ag^+$ ion-exchange process. Figure 7 shows the sensitivity values of the OWGs ion-exchanged for 15 min with different values of $[AgNO_3]$. These results showed that $S_{OWG}$ for high $[AgNO_3]$s were larger than those for low $[AgNO_3]$s, and that the loss was not too large for $[AgNO_3]<10$ mol%; $[AgNO_3]=5$ mol% was hence employed in the following experiments.

**Relative Sensitivity of the Composite OWGs.** To discuss the results of the sensitivity obtained, theoretical calculations were performed with Runge–Kutta method using Eq. 1. It was assumed that the distributions of $Ag^+$ and $K^+$ were Gaussian and the refractive index distribution in OWG layer, $n(x)$, was represented by a summation of the contributions from both ions,[12] and thus, Eq. 3 holds.

$$n(x) = n_s + \Delta n_{Ag} \exp\left(-(x/T_{\mathrm{eff,Ag}})^2\right) + \Delta n_K \exp\left(-(x/T_{\mathrm{eff,K}})^2\right) \quad (3)$$

Here $x$ is the distance from the surface towards the bulk, $n_s$ is the refractive index of the glass substrate, $\Delta n_{Ag}$ and $\Delta n_K$ are the refractive index changes caused by the ion-exchanged, and $T_{\mathrm{eff,Ag}}$ and $T_{\mathrm{eff,K}}$ are the effective thicknesses of each OWG layer. These parameters were fixed in the calculation as $n_s=1.515$, $T_{\mathrm{eff,K}}=1$ µm, $n_{Ag}=1.6$ and $n_K=1.5195$. Figure 8 shows detailed results of the measurements (symbols in the figure) and theoretical calculations (solid and dashed curves) of $S_{\mathrm{OWG}}$ of the composite OWG. The abscissa is square root of the time of ion-exchange in the $\mathrm{AgNO_3}$ bath ($t_{\mathrm{bath}}{}^{1/2}$) for the experimental results, and effective thickness of the $\mathrm{Ag^+}$-doped OWG ($T_{\mathrm{eff,Ag}}$) for the results of the calculation. Here, $T_{\mathrm{eff,Ag}}$ was assumed to be linear to $(t_{\mathrm{bath}})^{1/2}$ ; this assumption was successful for the $\mathrm{K^+}$-doped OWGs.[1] The maximum $S_{\mathrm{OWG}}$ observed was about 1400 $\mathrm{cm^{-1}}$ for the 545.5 nm monitoring and about 1300 $\mathrm{cm^{-1}}$ for 632.8 nm; such $S_{\mathrm{OWG}}$ values are almost the same as the calculated ones. Furthermore the calculation agreed with the experimental results that $S_{\mathrm{OWG}}$ values for 543.5 nm are larger than those for 632.8 nm.

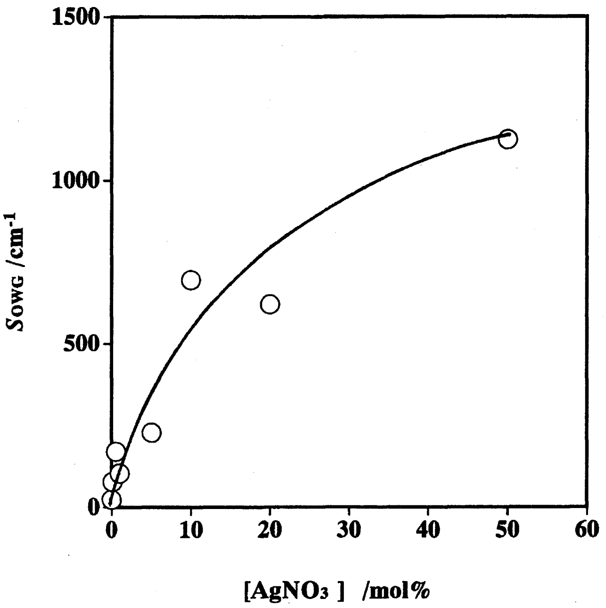

Fig. 7. The sensitivities ($S_{\mathrm{OWG}}$) of the composite OWGs prepared in different [$\mathrm{AgNO_3}$].

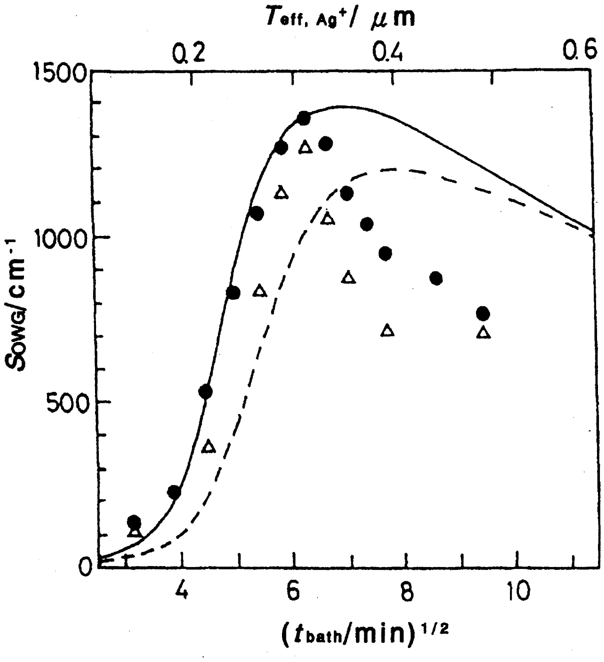

Fig. 8. Experimental and calculated sensitivities ($S_{\mathrm{OWG}}$) of the composite OWGs.[12] Experimental values: ● (at 545 nm) and △ (at 633 nm). Calculated values: solid curve (for 545 nm) and dashed curve (for 633 nm). $t_{\mathrm{bath}}$ is $\mathrm{Ag^+}$ ion exchanged time and $T_{\mathrm{eff,Ag}}$ is the effective thickness of the $\mathrm{Ag^+}$ ion exchanged layer.

The curve fitting was successful for small $t_{\mathrm{bath}}$ values, but was unsuccessful for large $t_{\mathrm{bath}}$ values. This discrepancy can be explained by considering that the diffusion rate of $\mathrm{Ag^+}$ depends on the $\mathrm{K^+}$ concentration during the ion-exchange process in the $\mathrm{K^+}$-doped region, that is, the $\mathrm{Ag^+}$ ions diffuse slowly in the $\mathrm{K^+}$-rich layer of the OWG, but diffuse quickly when they enter beneath the $\mathrm{K^+}$-doped layer. This consideration is based on our observation that a longer time was required to dope $\mathrm{Ag^+}$ into the $\mathrm{K^+}$-doped OWGs than into the glass substrate. As shown in Fig. 9, the distribution of $\mathrm{K^+}$ is Gaussian-like, and the $\mathrm{K^+}$ concentration is nearly constant in region I, and so are the diffusion coefficient of $\mathrm{Ag^+}$ and consequently the $T_{\mathrm{eff}}/t_{\mathrm{bath}}{}^{1/2}$ ratio. Thus, the curve fitting in Fig. 8 is justified for the short $t_{\mathrm{bath}}$ time regions. In region II and III, however, the diffusion rate of $\mathrm{Ag^+}$ increases as $\mathrm{K^+}$ concentration decreases with $x$, the thickness of OWG layer, and hence the $T_{\mathrm{eff}}/t_{\mathrm{bath}}{}^{1/2}$ ratio should be increased in these regions. Since we used constant $T_{\mathrm{eff}}/t_{\mathrm{bath}}$ ratio corresponding to the diffusion, the actual $T_{\mathrm{eff}}$ should be larger than that used in the calculation. Thus, it is reasonable that the curve fitting was unsuccessful for long ion-exchange times.

**Propagation Loss of Composite OWGs.** The propagation losses of the composite ion-exchanged OWGs are shown in Fig. 10. The loss is mainly caused by the $\mathrm{Ag^+}$-doped region because the losses of the $\mathrm{K^+}$-doped OWGs are very small and the values of the most highly sensitive samples (>1000 times/cm) were 3—5

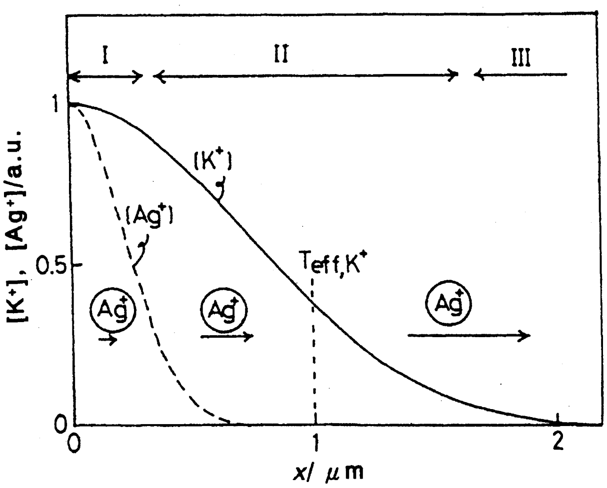

Fig. 9. Diffusion rate of $\mathrm{Ag^+}$ ion changes depending on $\mathrm{K^+}$ concentration in the OWG layer.[12] Region I, high [$\mathrm{K^+}$]; region II, medium [$\mathrm{K^+}$]; region III, low [$\mathrm{K^+}$]. The dashed curve is [$\mathrm{Ag^+}$] for maximum $S_{\mathrm{OWG}}$.

dB cm$^{-1}$. The losses were low in short ion-exchange times, but became large with ion-exchange time, probably because the surface roughness became severe after the long time ion-exchange.

**Annealing Property.** Stability of the sensitivity in high temperature atmospheres may be necessary for OWGs to be used in some surface spectroscopic measurements, and thus we examined the annealing property of the composite OWGs. Figure 11 shows the changes of relative sensitivity of the composite OWGs annealed for different periods of time. It was found that the composite OWG is unstable when heated at 400 °C. This is likely because the further diffusion of both the $K^+$ and the $Ag^+$ ions occurred at this temperature. The $Ag^+$-doped OWG layer became thicker and the surface refractive index became smaller, and thus, the surface relative sensitivity decreased as annealing time increased.

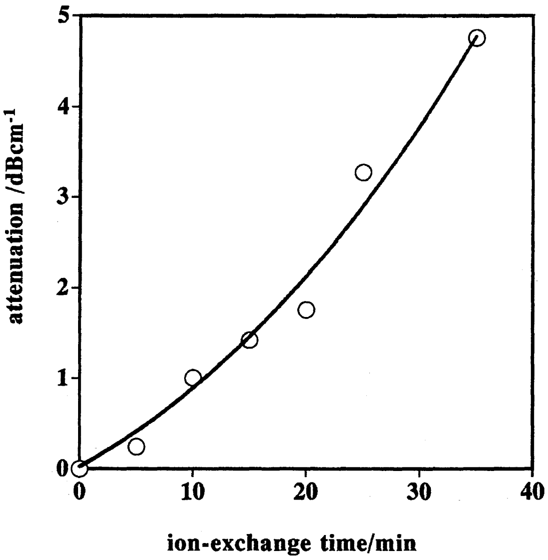

Fig. 10. The attenuation of the composite OWGs prepared in 5 mol% $AgNO_3$ for different periods of time.

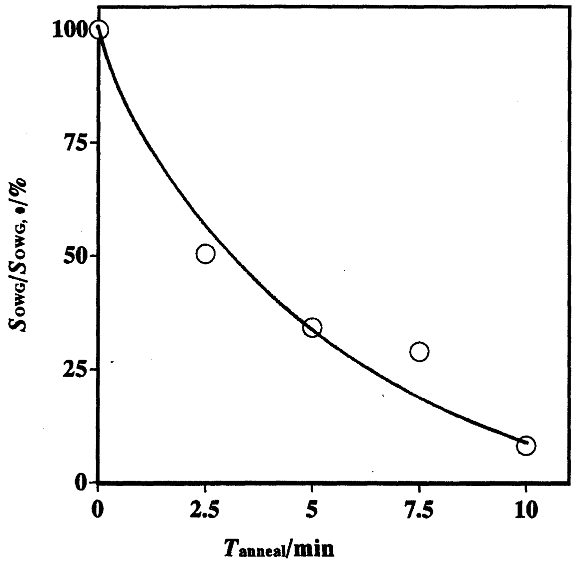

Fig. 11. The changes of relative sensitivities of the composite OWGs annealed. $S_{OWG,0}$ is the relative sensitivity of the OWG before annealing.

**Effect of UV-Irradiation.** In a weathering test of the OWGs, we have examined the effects of UV-irradiation on several kinds of glass OWGs, and sometimes found large decreases of the guided light. Although the details of this phenomenon will be discussed elsewhere, we examined here whether or not the UV-irradiation has effects on the composite ion-exchanged OWG, by irradiating the OWGs with 254 nm UV light. Figure 12 shows the result of the UV-irradiation upon the composite OWG. We observed that the UV-irradiation caused attenuation of the guided light, and the change was reversibly recovered for short irradiation time (e.g. 10 s), but was not sufficiently reversible after a long time irradiation (e.g. 10 min). The UV-irradiation probably caused some structure changes or induced color centers in the glass OWG. Detailed investigation is now under way.

## Conclusions

We have described the preparation and properties of the $Ag^+/K^+$ composite ion-exchanged OWGs designed for surface spectroscopy. They showed low loss and high sensitivity, the $S_{OWG}$ of the $Ag^+$-doped region was more than 1000 times per unit length compared with spectroscopic measurement with normal incidence of monitoring light; but were unstable at high temperature (>400 °C) and against UV-irradiation at 254 nm.

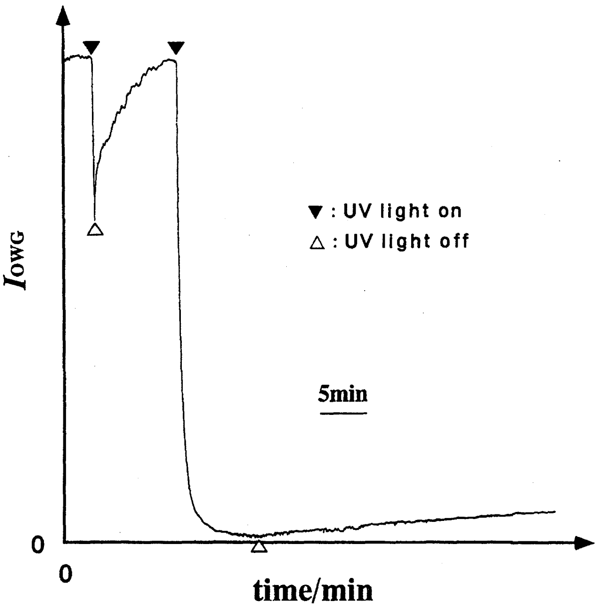

Fig. 12. The effect of UV-irradiation upon composite OWG. The intensity change of the guided light was reversibly recovered after a short time (10 s) irradiation, and irreversible after a long time (10 min) irradiation.

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