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Characterization of secondary silver ion exchange in potassium-ion-exchanged glass waveguides

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Abstract. Local enhancement of refractive index in potassium-ion-exchanged optical waveguides in glass is of interest for realization of low-loss bends and intersections and more complex structures such as gratings for reflection and phase-matching. Local enhancement may be realized through subsequent ion exchange with an ion having higher polarizability, such as silver. However, in order to design such structures, the diffusion of silver ions into potassium ion-exchanged waveguides must be characterized. In this paper, we present and compare diffusion profiles and coefficients of silver ions in soda-lime glass and in potassium-ion-exchanged waveguides in this glass.

1. Introduction

Potassium-ion-exchange is a well-developed process for fabrication of passive optical-fibre-compatible waveguide components in glass, having the advantages of cheap base materials and processing, and good chemical and physical ruggedness [1,2]. The functionality of this system has been considerably enhanced by the demonstration of planar waveguide lasers [3], and applications as diverse as chemical sensing [4] and wavelength demultiplexers for telecommunications [5] are being pursued. Local enhancement of the refractive index of potassium-ion-exchanged waveguides may be exploited in waveguide bends and intersections [6] and, for example, in periodic structures for optical phase-matching [7] and to couple two dissimilar waveguides [8]. As silver ion exchange in glass takes place at a much lower temperature than that of potassium [1], silver ion exchange may potentially be used after potassium ion exchange without significantly affecting the distribution of the potassium ions [9]. The effective 'masking' of silver ion exchange by previous potassium ion exchange has been reported previously [10, 11], but this process must be fully quantified to allow the design and realization of waveguide devices utilizing multiple diffusion.

In this paper, silver ion exchange in potassium-ion-exchanged glass is characterized, and effective diffusion coefficients given. Results for single-step silver and potassium ion-exchange processes are presented first, in order to allow comparison with the two-step diffusion process and with previous work elsewhere [12–16]. The glass used in this work is standard soda-lime glass, which

is rich in sodium, inexpensive, and readily available in the form of microscopic slides. Much work in this field has been carried out using optical quality glasses such as BK7 [15], which yield substantially lower waveguide losses; however, in many applications, such as fabrication of disposable chemical sensors, state-of-the-art waveguide losses are not required.

2. Ion exchange in glass

The refractive index of a multicomponent glass depends upon the type and concentration of alkali ions present. Optical waveguides may be fabricated by replacing alkali ions present in the bulk glass with others which

(i) exhibit higher polarizability,
(ii) result in compaction of the glass matrix, or
(iii) induce stress in the exchanged regions,

all of which result in an increase in refractive index with respect to the substrate. Soda-lime silicate glasses are often used for optical waveguide applications because of their chemical durability, low cost and ready availability. In a simple ion-exchange process a monovalent cation from a glass network modifier, such as Na_2O, exchanges with another monovalent cation, usually from a molten salt. The depth of this exchange is dependent upon the diffusion coefficient (D) of the incoming ion in the bulk glass at the exchange temperature (T) and the duration of the exchange (t), according to Fick's law [17]. This results in a concentration profile approximately following a complementary error function with a depth, $d = 1.28(Dt)^{0.5}$, at $1/e$ peak concentration.

Walker *et al* [18] observed disagreement between the theoretical ERFC profile and experimental results, and explained this in terms of a mismatch between the diffusion coefficients for sodium and silver ions. However, their results were obtained using the indirect inverse WKB method, and are applicable only for diffusions of less than 15 min duration. Giallorenzi [19] and Ramaswamy *et al* [2] have used direct methods such as use of an electron microcrobe to determine concentration profiles of silver ions introduced by ion exchange in soda-lime and borosilicate glass for longer periods, and have found that the complementary error function fits their data well.

The refractive index profile is assumed to replicate approximately the concentration profile of the exchanged ions [20]. As network modifiers contribute only in a minor way to the glass structure, the basic structure of the glass is left unchanged while the concentration profile, and hence the refractive index, may be increased or decreased. The refractive indices and dimensions of ion-exchanged optical waveguides may be readily varied by adjustment of the nature and concentration of incoming cations in the salt melt [2, 12] and the time and temperature of exchange [2, 13]. Potassium ion exchange is a suitable choice for fabrication of single-mode waveguides with dimensions comparable to those of optical fibres, due to the small peak index increase resulting, the relatively long exchange times, which allow greater processing latitude, and the low waveguide losses achieved [13]. Silver ions exchange rapidly into unmodified soda-lime silicate glass when compared with potassium ions, and result in a large index increase due to their high electronic polarizability. Silver ion exchange may therefore be suitable for local modification of the refractive index of potassium-ion-exchanged waveguides, as large index enhancements may be possible without significantly altering the diffusion profiles of the existing waveguides. The diffusion coefficient of silver ions into glass in which a substantial proportion of the sodium ions has already been replaced with potassium ions will be substantially different from that in the original glass [11]. Before any devices may be designed, this must be quantified by determining the diffusion coefficient of silver ions in untreated and in potassium-ion-exchanged substrates.

3. Experimental method

3.1. Sample preparation

The substrates used were soda-lime silicate glass cover slides (ROWI), which were cleaned in 1,1,1-trichloroethane, acetone and fuming nitric acid, rinsed in de-ionized water and baked at 120 °C for 30 min. Throughout this study the potassium nitrate bath used was maintained at 338 ± 2 °C and the silver nitrate bath was maintained at 240 ± 2 °C, in separate silica beakers. Three series of diffusions, each comprising eight samples, were performed as follows.

(i) Potassium ion exchange in untreated substrates.

(ii) Silver ion exchange in untreated substrates.

(iii) Silver ion exchange in substrates previously exchanged in KNO_3 for 120 min.

For each series the exchange durations ranged from 10–120 min. A duration of 120 min was chosen for the preliminary potassium ion exchange in series (iii), as this results in low-loss channel waveguide device operation over our wavelength range of interest (450–900 nm). The silver melt temperature was chosen to be low in order to reduce the diffusion coefficient, leading to greater control over processing in subsequent device fabrication. The melt was not stirred in this study, and substrates were held just above the melts for 5 min before ion exchange, to raise their temperature close to that of the melt before immersion.

3.2. Sample characterization

After the ion-exchange process described above, each sample was sawn to expose a diffusion cross section at least 5 mm away from the edges of the substrate. This edge was then optically polished normal to the substrate surface to allow analysis by energy dispersive spectrometry (EDS) [21]. The EDS technique may be used to analyse the energy spectrum of x-rays generated when an electron beam irradiates a sample, and hence to determine atomic concentrations. Spatial resolution depends upon the scattering of electrons within the material, and is typically of the order of 1 μm.

In this study, concentration profile measurements were made using a JEOL JSM 6400 scanning electron microscope (SEM) and TRACOR series II x-ray and image analysis system. The electron beam energy used was 15 keV, resulting in an estimated lateral resolution of 0.8 μm [21]. Atomic concentrations of sodium, potassium and silver were measured at 0.8 μm intervals normal to the polished edge (which is itself perpendicular to the substrate surface) and converted into weight per cent of oxide in each case for comparison with other workers' results.

4. Results and discussion

4.1. Composition of substrate material

One sample of untreated substrate material was cleaned and analysed for concentration of oxides. Table 1 gives the composition of the glass used in this study before any ion-exchange processing, together with that reported by workers elsewhere in other soda-lime glasses for purposes of comparison.

Table 1. Concentration of oxides in initial substrate glasses.

Compound	Weight per cent	References			
		[14]	[15]	[16]	[20]
SiO$_2$	74.0	73.10	72.25	72.31	Major constituent
Na$_2$O	11.8	13.8	14.31	14.33	12.00
CaO	6.1	8.60	6.40	6.44	8.00
MgO	5.1	4.00	4.30	4.31	2.00
K$_2$O	0.0	0.04	1.20	1.21	—
Al$_2$O$_3$	2.7	0.10	1.20	1.22	4.0
Traces	0.3	0.41	0.33	0.18	—
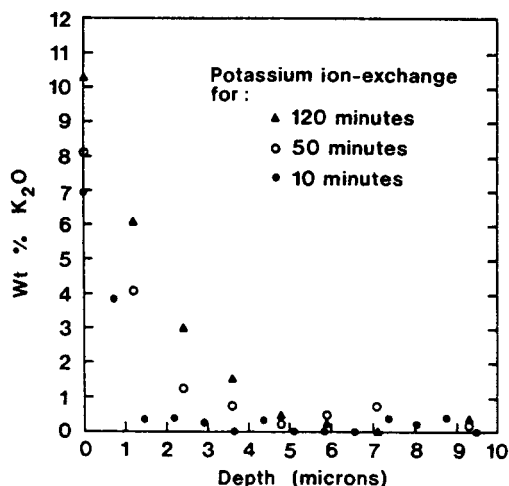
Figure 1. Thermal diffusion profiles of potassium oxide in soda-lime glass.

4.2. Potassium ion exchange in untreated substrates

Unprocessed measured concentration profiles for potassium ions in substrates ion-exchanged in KNO$_3$ measured in this way indicated that both the depth of diffusion and peak surface concentration of potassium ions increased as the diffusion time increased. These profiles for potassium ions in samples exchanged for 10, 50 and 120 min are given in figure 1. Fick's law shows that peak surface concentration should not change with time, and it was found that the complementary error function (ERFC) was not a good model of the observed data due to the depth resolution of the measurement being comparable to the diffusion depths being measured. In order to determine real diffusion depths from the data it was necessary to model our data as an ERFC convolved with a 0.8 μm Gaussian due to the 0.8 μm spot size of the excited sample in the EDS measurement.

The initial measured concentration profile for a 120 min potassium ion exchange is compared with an ERFC convolved with a Gaussian of width 0.8 μm in figure 2. It is observed that the data agree well with theory, confirming that the complementary error function accurately describes the diffusion profile. In the remainder of this paper, the unprocessed data will be presented and the parameters deduced from this data, for example the depth of diffusion and surface concentration, will be those of the ERFC concentration profile, which,
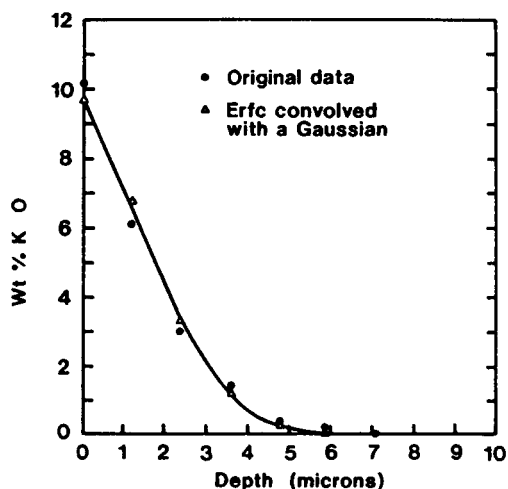
Figure 2. Thermal diffusion profiles of a 120 min potassium ion exchange in soda-lime glass compared with an ERFC convolved with a Gaussian of width 0.8 μm.
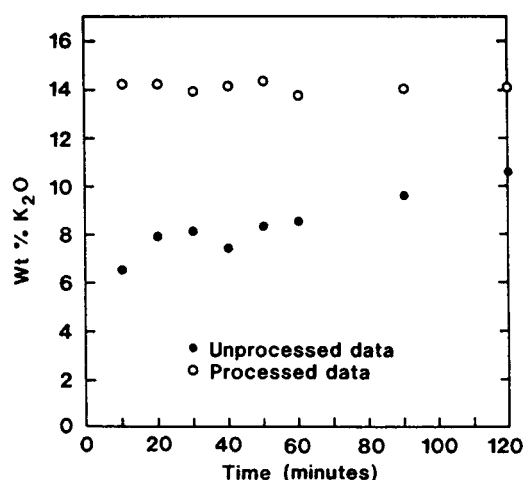
Figure 3. Surface concentration of potassium oxide as a function of diffusion time.

when convolved with the Guassian probe of 0.8 μm width, yields the best fit to that data.

Figure 3 shows the surface concentration of potassium oxide, determined in this way, plotted against potassium ion exchange duration. It can be seen that surface concentration remains constant independent of diffusion time. A real surface concentration of 14.1 wt% K$_2$O was recorded for all of our potassium-diffused samples.

The depth at which the concentration has fallen to 1/e of its surface value, d, using the above procedure, is plotted against the square root of diffusion time in figure 4. The diffusion coefficient of potassium ions in this glass at 388 °C, D_K, is found to be (1.51 ± 0.33) × 10^{-15} m^2 s^{-1} by taking a least squares fit to this data and assuming an ERFC concentration profile. Our value for the diffusion coefficient compares with that of Yip [16], who obtained a value of 1.08 × 10^{-15} m^2 s^{-1} for the diffusion coefficient for potassium exchange at 385 °C in soda-lime glass.
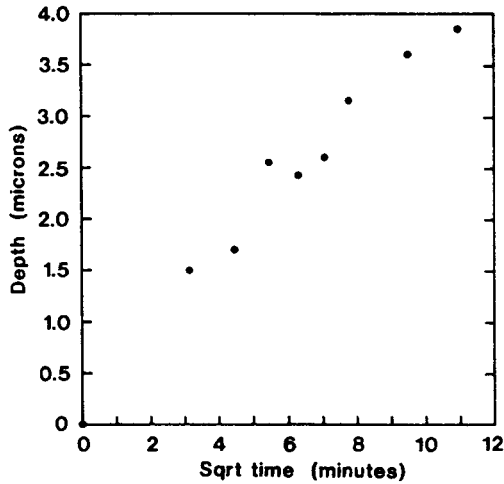
Figure 4. Penetration depth as a function of time for potassium diffused in soda-lime glass.
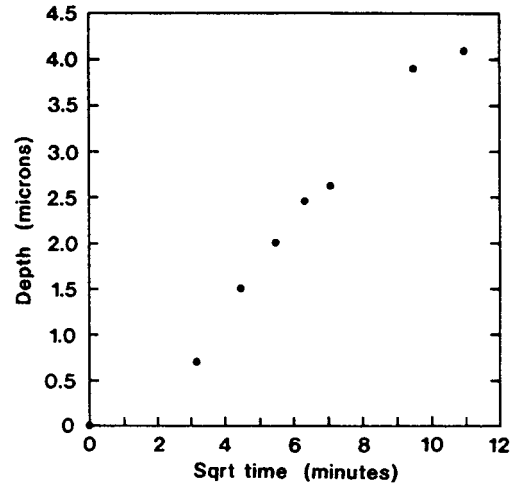

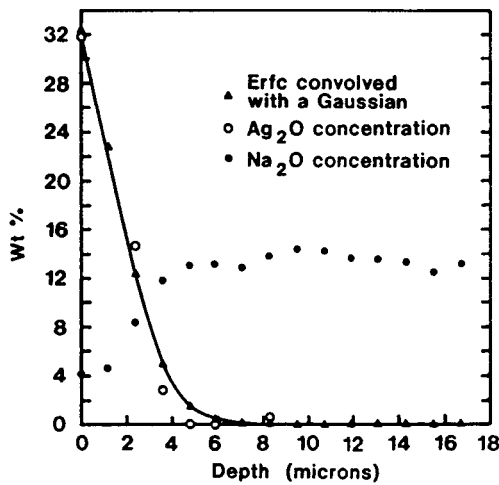**Figure 6.** Penetration depth as a function of time for silver diffused in soda-lime glass.

Figure 5. Thermal diffusion profiles of a 120 min silver ion exchange in soda-lime glass.

Figure 7. Penetration depth as a function of time for silver diffused in potassium-ion-exchanged waveguides.

4.3. Silver ion exchange in untreated substrates

Concentration profiles for silver and sodium ions in samples ion-exchanged in $AgNO_3$ were obtained by EDS as above, and figure 5 shows unprocessed data for a diffusion time of 120 min. The silver oxide surface concentration found from the 'best-fit' ERFC corresponds to a concentration of 26.9 wt% and is equivalent to an increase of 3.75×10^{21} ions cm^{-3} in the surface region, with a corresponding decrease in the number of sodium atoms. It can be seen that the ERFC is a good fit to the data. The data are summarized in figure 6, where the diffusion depth, d, is plotted against $t^{0.5}$. The diffusion coefficient for silver ions in the untreated substrate glass at 240 °C is thus determined to be $D_{Ag} = (1.63 \pm 0.13) \times 10^{15}$ m^2 s^{-1}, from the slope of the line of best fit as described above compared with $D_{Ag} = 1.8 \times 10^{-16}$ m^2 s^{-1} at 225 °C in a soda-lime glass with a similar initial content of sodium oxide [19].

4.4. Silver ion exchange in potassium-ion-exchanged substrates

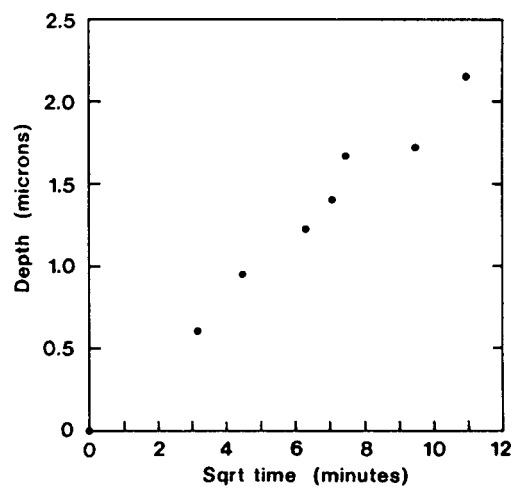Concentration profiles of sodium, potassium and silver

ions were obtained for samples in which silver ion exchange was carried out in samples previously potassium-ion-exchanged for 120 min. A graph of the diffusion depth, d, of silver ions against the square root of diffusion time for these doubly-diffused samples is given in figure 7. A least-squares fit to these data yields a coefficient for the diffusion of silver ions in potassium-ion-exchanged glass at 240 °C, D'_{Ag} of $(3.92 \pm 1.10) \times 10^{-16}$ m^2 s^{-1}. The reduction in the diffusion coefficient, D, due to the previous potassium ion exchange is clear, and the reduced range of diffusion depths results in greater uncertainty in determining the slope of this curve. The presence of potassium ions in the substrate glass due to previous potassium ion exchange has reduced the diffusion coefficient of silver ions in glass by a factor of approximately four.

Comparison of the potassium ion concentration profiles before and after a 120 min silver ion exchange in figure 8 shows that the potassium ion concentration profile is not significantly altered by the silver ion exchange.

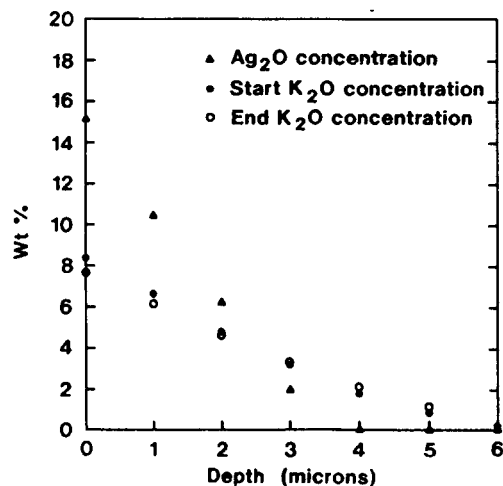Comparison of the sodium ion concentration profiles in figure 9 for substrates ion-exchanged in $AgNO_3$

Figure 8. Deconvolved thermal diffusion profiles of silver and potassium oxide when silver is diffused in potassium-ion-exchanged waveguides.
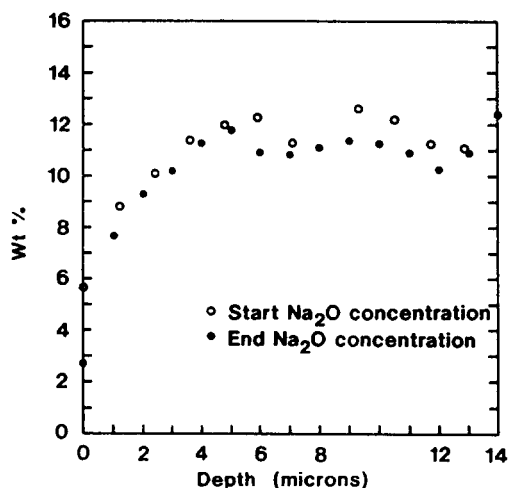

Figure 9. Thermal diffusion profiles of sodium oxide when silver is diffused in potassium-ion-exchanged waveguides.

shows that the surface concentration of sodium has been reduced further by the secondary silver ion exchange. Processed data shows that the surface concentration has fallen from initially 12.2 wt% before any diffusion to 5.7 wt% after potassium diffusion and then to 3.0 wt% after the secondary silver diffusion. The total numbers of silver and sodium atoms remain constant upon exchange from an examination of the observed EDS data. This is consistent with charge neutrality being maintained in the glass as a silver ion can only enter the network matrix upon expulsion of either a sodium or a potassium ion.

Comparison of figure 6 with figure 7 clearly shows the reduction of the diffusion coefficient due to the presence of potassium ions, and from figures 5 and 8 the reduction in the surface silver ion concentration obtained. The unprocessed data shows that after 120 min ion exchange in $AgNO_3$, subsequent to 120 min potassium ion exchange, the surface silver oxide concentration has reached only 15.8 wt% compared with 31.8 wt% in the untreated samples. Processing the data as described above results in deduced values of surface concentration of 15.1 wt% and 26.9 wt% respectively. The

reduced self-diffusion coefficient and reduced surface concentration are due to the lower mobility of potassium ions in this glass compared with the sodium ions that have been replaced. Chartier [11] noted this hindrance of silver ion diffusion in potassium-ion-exchanged regions, but did not examine the concentration profiles and obtain diffusion coefficients.

4.5. Group II ion diffusion

Within experimental error, no depletion of group II ions was observed in all three processes in which 25 ion-exchange-diffused samples were studied. This conclusion is in agreement with Miliou [15], Yip [16] and Giallorenzi [19]. We found that the calcium content before diffusion was 5.9 ± 0.4 wt% and the magnesium concentration 4.6 ± 0.8 wt%. After diffusion the surface concentrations for calcium and magnesium were found to be 5.4 ± 0.9 wt% and 4.3 ± 0.6 wt% respectively.

5. Conclusion

Multiple ion exchange in glass has been proposed to realize waveguide devices such as gratings and low-loss intersections [7,9]. While the reduction of the rate of silver ion exchange in glass in which an optical waveguide has already been formed by potassium ion exchange has been observed previously [11], the design and realization of devices using such multiple diffusions has been hampered by the lack of quantitative data on the diffusion coefficients and resulting concentration profiles.

In this paper a detailed quantitative analysis of these ion exchange processes has been carried out using EDS [21]. It was found that, to model the experimental data correctly, it was necessary to convolve a complementary error function representing the real diffusion profile with a Gaussian of 0.8 μm width due to the excitation spot size from the electron probe beam. The diffusion coefficient of silver ions in potassium-ion-exchanged soda-lime silicate glass at a temperature of 240 °C was reduced by a factor of approximately four, when compared with such an exchange in untreated glass. The diffusion coefficients are $(3.92 \pm 1.10) \times 10^{-16}$ m^2 s^{-1} and $(1.63 \pm 0.13) \times 10^{-15}$ m^2 s^{-1} for silver diffused in potassium-ion exchanged glass and into the base glass, respectively. It was also found that the processed surface concentration of silver oxide at the surface of these samples after exchanges of 120 min was reduced from 26.9 wt% to 15.1 wt% correspondingly. The potassium ion concentration profile was unmodified below the penetration depth of the silver ions after the secondary silver ion exchange. The concentrations of group II ions remained unchanged in all samples.

It has previously been demonstrated that, in masked regions, potassium-ion-exchanged waveguides appear unchanged by immersion in a silver nitrate melt at 225 °C [9]. The results presented in this paper show that silver ions may be incorporated into unmasked regions

of potassium-ion-exchanged waveguides, allowing local enhancement of the refractive index of the waveguide without significant perturbation of the remainder of the optical circuit for controllable imprinting of fine structure on the basic waveguide design, and provide quantitative data for design and realization of devices using double diffusion.

Acknowledgments

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