

Copper-ion-doped channel waveguide by two-step ion exchange in silicate glass substrate

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A process to manufacturing of copper-ion-doped channel optical waveguide in glass substrate is presented, which is composed of two stages: copper-ion-doped layer formation in glass substrate surface, and subsequent channel waveguide fabrication in the copper-ion-doped layer by Ag^+/Na^+ ion exchange. This approach circumvents high-temperature requirement in the stage of channel waveguide formation, and therefore make it viable to fabricate copper-ion-doped channel waveguide by melt salt ion exchange; furthermore, by employing Ag^+ for the channel waveguide formation, the performance of copper-ion-doped optical waveguide is expected to be optimized with an extra degree of freedom.

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1. Introduction

Ion exchange is currently regarded as one of the most promising processes for the fabrication of integrated optical waveguide devices in glass substrates. The primary factors contributing to this outcome are its industrial scalability, cost-effectiveness, as well as superior compatibility with a wide spectrum of glass compositions. The origins of ion-exchange glass-based optical waveguide technology can be traced back to 1972, when the first research paper on this subject was published [1]. In the subsequent decades, the demand for integrated optical devices in optical communication networks, combined with the unwavering dedication of numerous scientists and engineers worldwide, contributed to a rapid development in integrated optical waveguide devices based on ion-exchanged glass. The development of integrated optical splitters is a prime example of research and application in the field. Presently, glass-based integrated optical splitters fabricated using ion-exchange technology have been extensively adopted in optical communication networks and evince considerable advantages in terms of performance and cost. Furthermore, researchers anticipate the fabrication of lasers, amplifiers, non-linear optical devices, and other functional waveguide devices on planar glass waveguide chips by utilizing of ion-exchange technology. This would be of further benefit in enhancing the functionality and versatility of optical information systems [2-6].

Researchers in the field of integrated photonics have been demonstrating a keen interest in studies on copper-ion-doped optical waveguides in glass substrates [7-22]. The primary motivation for the investigation of waveguide fabrication technology stems from its potential

applications in two distinct domains. The initial domain encompasses the fabrication of functional integrated photonic waveguide devices, green-blue emitting waveguide lasers [8], and nonlinear optical waveguide devices [7,9], to cite but a few examples. The second potential application of these materials lies in their potential use as large-size waveguide panels for board-level optical interconnects [6,10].

As with Ag^+ -doped optical waveguide fabrication, two primary approaches have been identified for the fabrication of copper-ion-doped waveguides: melted salt ion exchange [11-16] and electric field-assisted metal film diffusion [17-22]. Given the superior contact conditions offered by solid-liquid phase reactions in comparison to solid-solid phase reactions, the melted salt ion exchange method is the highly preferred approach for the fabrication of fine waveguide structures and the mitigation of waveguide defects. However, as Kohei Kadono has noted [23], the fabrication of copper-ion-doped channel waveguides using this method poses significant challenges. These challenges primarily stem from the difficulty in selecting chemically stable copper-containing molten salt systems that can be melted at a reasonably low temperature. A mixture of CuSO_4 and Na_2SO_4 salts is most frequently employed as a copper ion source. However, ion exchange must be carried out at a temperature higher than the eutectic point of the two components (approximately 537 °C), which exceeds the operating temperature range of the frequently used aluminum mask film. Consequently, the mask film is susceptible to damage during the waveguide formation process. Jarmila Spirkova et al. [11, 15] have employed a ZnCl_2 and CuCl mixture as a copper ion source, given that its eutectic point is considerably lower (below 240°C). However, experimental

investigations conducted in our laboratory have demonstrated that the glass surface is susceptible to significant erosion in the melt due to the dissolution of metal oxides in molten ZnCl_2 . Additionally, CuCl exhibits a high level of sensitivity to both air and moisture, and is prone to oxidization at temperatures above room temperature, resulting in the formation of higher-valent copper salts. Consequently, despite the publication of numerous articles on slab waveguide manufacturing, there is a paucity of literature addressing copper-ion-doped channel waveguides manufactured by melted salt ion exchange. To date, the vast majority of reported copper-ion-doped channel waveguides have been manufactured using electric field-assisted copper film diffusion [17–21].

In order to capitalize on the full potential of the molten salt ion exchange process, a process for copper-ion-doped channel waveguides is presented in this paper. This process is comprised of two stages: the initial stage is copper-ion-doping, and the subsequent stage is channel waveguide formation. The initial stage involves the formation of a planar copper-ion-doped layer on the surface of the glass substrate. This layer is created through the application of molten salt ion exchange in copper salts. Subsequently, in the second stage, a channel waveguide core is formed in the copper-ion-doped layer by Ag^+/Na^+ ion exchange. The present paper delineates the fabrication and characterization of a copper-ion-doped optical waveguide.

2. Method and experiment

A soda-lime glass, manufactured by CSG Holding Co., China, with an approximate Na_2O content of 14.7 mol%, was utilized as the substrate material for the fabrication of the copper-ion-doped channel waveguide. The two-stage process utilized for the copper-ion-doped channel waveguide fabrication is depicted schematically in Fig. 1. In the first stage, a soda-lime glass chip is immersed in a salt mixture comprising CuSO_4 and Na_2SO_4 with a eutectic composition (55 mol% CuSO_4 and 45 mol% Na_2SO_4) at 550 °C within a silica container situated in a muffle furnace for a duration of 15 minutes. During this process, a planar copper-ion-doped layer is formed in the surface of the glass substrate. The second stage involves the formation of a channel waveguide in the copper-ion-doped layer by Ag^+/Na^+ ion exchange in an AgNO_3 and NaNO_3 mixture (AgNO_3 content 3 mol %) at 380 °C for 30 minutes. The waveguide structure of the channel is delineated by photolithographically defined windows with width of 3.0 μm in a vacuum-evaporated aluminum mask film on the glass substrate surface. During this stage, silver ions are exchanged with sodium ions in the copper-ion-doped layer and diffuse into it to form a region with a high refractive index, which constitutes the core of the channel optical waveguide.

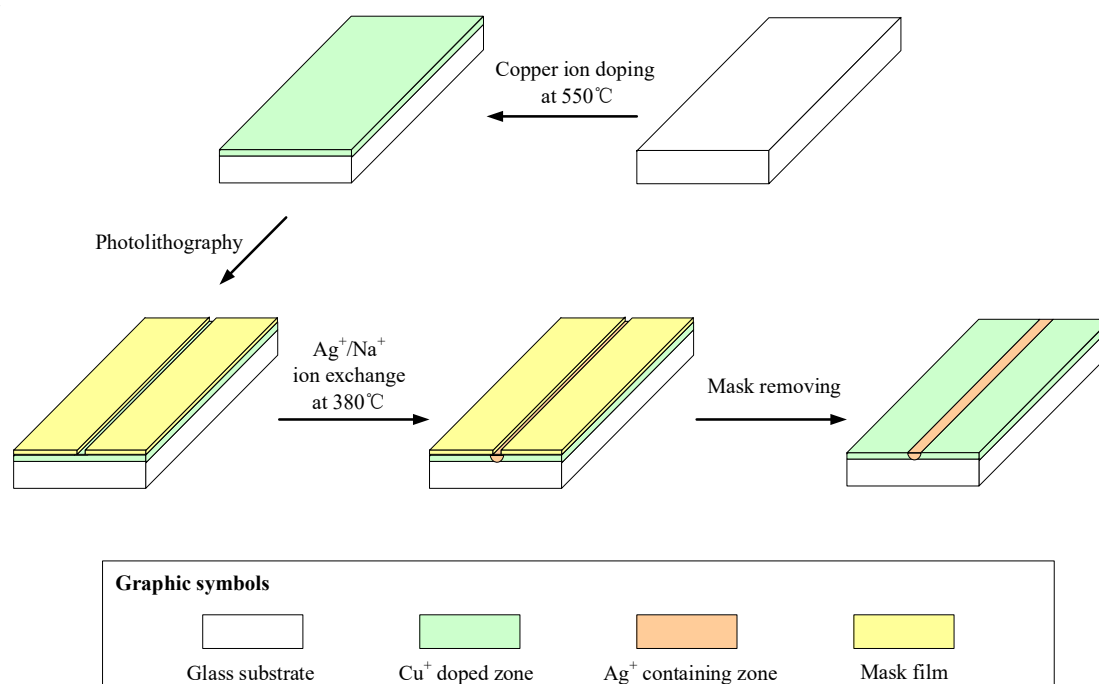


Fig. 1. Manufacturing process of Copper-ion-doped channel waveguide in glass substrate (colour online)

Subsequent to the lapping and polishing of the waveguide chip end surfaces, an electron probe microanalyzer (EPMA) equipped with a wavelength-dispersive X-ray spectrometer (WDS) was utilized for the optical waveguide channel cross-section characterization.

The optical intensity pattern of the fabricated channel optical waveguide is observed using a CCD camera. The insertion loss of the fabricated channel waveguide at a wavelength of 1550 nm is measured by butt-coupling two single-mode fibers to the two ends of the optical

waveguide chip under test. The transmission loss of the optical waveguide and the optical waveguide coupling loss with a single-mode optical fiber are determined by the cut-back method.

In order to investigate the photoluminescence spectrum of the copper-doped zone subsequent to the introduction of Ag^+ (as in the case of the channel waveguide core), a copper- and silver-doped sample is examined using a Hitachi F-4500 fluorescence spectrophotometer. This sample was prepared using the same approach as described above, except that a mask film was not applied in the Ag^+/Na^+ ion exchange step.

3. Results and discussion

The backscattering electron (BSE) image of the cross section of the channel optical waveguide under EMPA is displayed in Fig. 2. As illustrated in the figure, a high brightness layer is present on the surface of the glass substrate, within which an even higher brightness zone is embedded. According to the optical waveguide chip manufacturing process stated above, the high brightness layer can be identified as a copper-doped region, and the zone of even higher brightness as a silver-ion-doped region formed by Ag^+/Na^+ ion exchange. The element distribution maps of Ca, Na, Ag, and Cu, as scanned by EMPA, are presented in Fig. 3. It is evident from these images that a copper-doped layer with a thickness of approximately $10.0\ \mu\text{m}$ is present in the surface layer of the glass substrate. Within this layer, there is an Ag^+ diffusion region measuring $10.0\ \mu\text{m}$ by $8.0\ \mu\text{m}$ that is embedded. As illustrated in Fig. 3, the content of calcium and sodium elements exhibits a decline in the copper-

doped layer. Consequently, it can be deduced that Cu^{2+} (and/or Cu^+) / Ca^{2+} and Cu^{2+} (and/or Cu^+) / Na^+ ion exchange occurs concurrently during the copper doping process. It is noteworthy that, due to the elevated processing temperature of copper ion doping, calcium ions within the glass matrix exhibit high mobility and thus diffuse out from glass surface layer and into the molten salts. A discernible decline in sodium levels is observed, while the copper concentration within the Ag^+ diffusion region remains unchanged. Consequently, the predominance of Ag^+/Na^+ ion exchange in the formation of the channel optical stage is attributed to the diminished mobility of copper ions at the processing temperature.

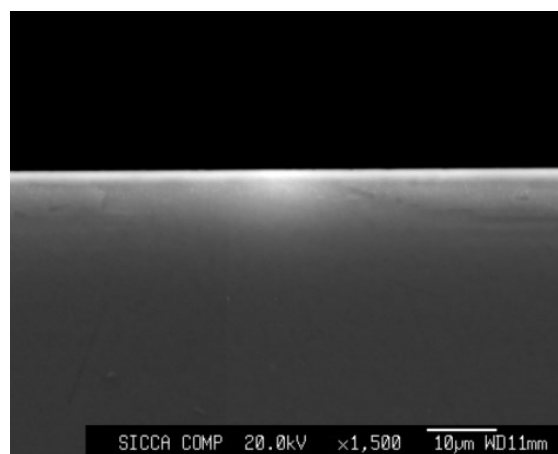


Fig. 2. BSE image of cross-section of channel waveguide under EMPA

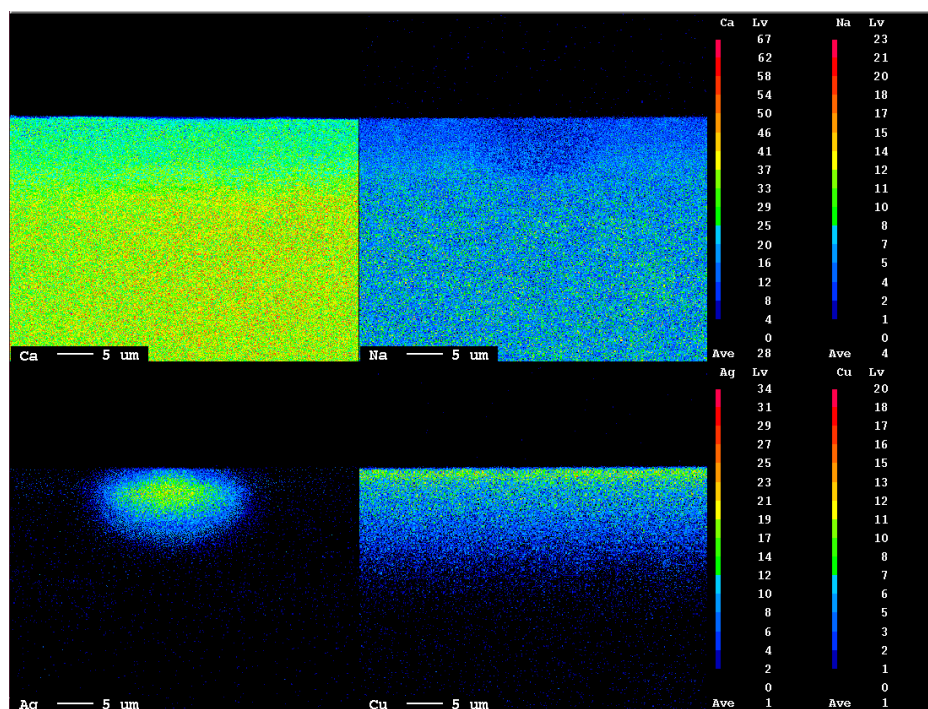


Fig. 3. Element distribution maps of Ca, Na, Ag and Cu scanned by EPMA (colour online)

The launching of a laser with a wavelength of 1550 nm was accomplished by means of butt coupling, with the implementation of a single-mode fiber. The output end face of the optical waveguide was imaged using a microscopic objective, and the resulting optical field is shown in Fig. 4. It can be concluded that the Ag^+ diffusion region functions as the waveguide core due to its higher refractive index compared to that of the glass substrate and the copper diffusion layer.

The figure illustrates the dependence of the insertion loss of the fabricated optical waveguide on its length. Employing the linear fitting method, the transmission loss of the channel waveguide was determined to be approximately 0.33 dB/cm, and the coupling loss with the single-mode fiber was found to be 0.62 dB/facet.

It is noteworthy that the transmission and coupling losses could be further mitigated through the optimization of the fabrication parameters of the channel waveguide in an experimental setting. The photoluminescence spectrum of the glass substrate co-doped with copper and silver, with an excitation wavelength of 292 nm, is shown in Fig. 6. In addition, the figure presents a comparison of the fluorescence spectra of a copper-ion-doped glass substrate and soda-lime glass in the absence of doping ions. A broad luminescence peak, centered at 500 nanometers, is evident. This peak corresponds to the emission of copper ions (Cu^{2+}) within the glass substrate, which has undergone co-doping with copper and silver. This peak demonstrates a strong resemblance to that of a copper-ion-doped glass substrate. This finding indicates that copper ions retain their luminescence properties following an Ag^+/Na^+ ion exchange, a property that is highly desirable for applications in light-emitting integrated waveguide devices.

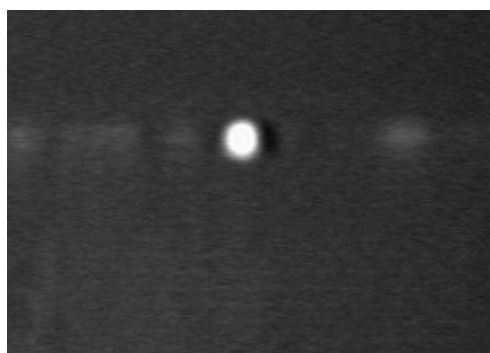


Fig. 4. Optical field pattern of copper doped channel waveguide

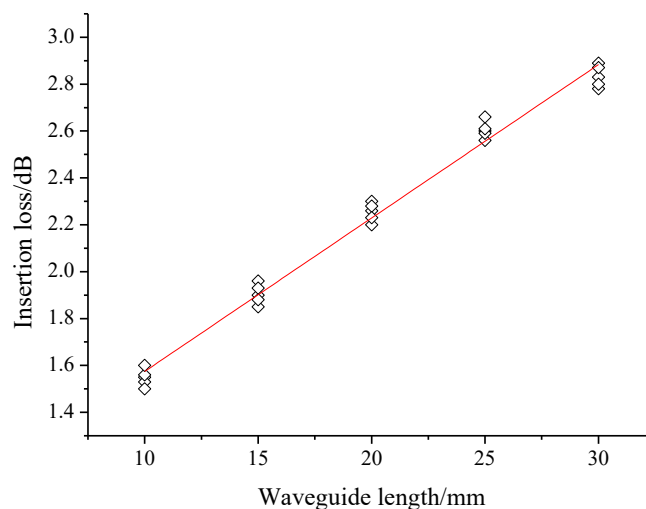


Fig. 5. Dependence of channel waveguide insertion loss on its length

In the conventional approach to fabricating copper-ion-doped waveguides for use in integrated light-emitting devices, the copper ions diffused into the glass substrate play two roles: they emit blue-green light as active ions in the glass matrix and modify the refractive index of the glass matrix as high-polarizability ions, to form the channel optical waveguide. Conversely, the prevailing waveguide fabrication method entails the deliberate introduction of copper ions into the glass, thereby serving as active ions. This process concomitantly results in the modification of the glass's refractive index. Additionally, silver ions are introduced as high polarizability ions, a strategy that further enhances the refractive index of the glass and leads to the formation of a channel waveguide within the copper-ion-doped layer. The process of copper ion doping of the glass matrix is conducted at an elevated temperature in the absence of a masking film. In contrast, the formation of the channel waveguide by Ag^+/Na^+ ion exchange is conducted at a substantially lower temperature, a condition that is safe for the aluminum mask. Consequently, this method circumvents the high-temperature requirement in the channel waveguide formation process, thereby facilitating channel waveguide fabrication and representing a substantial technological advancement.

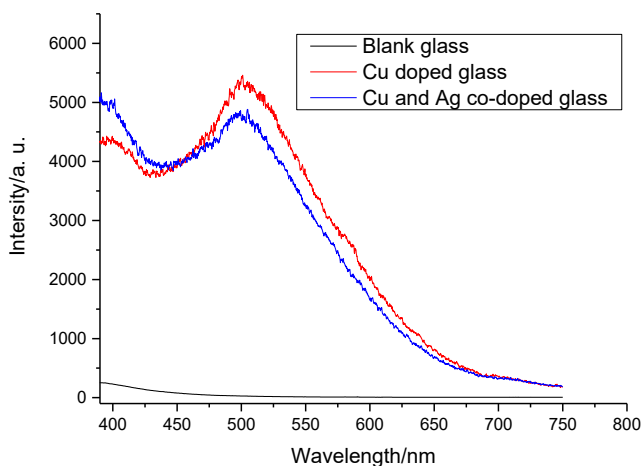


Fig. 6. Photoluminescence spectrum of Copper-ion-doped glass substrate, and copper and silver co-doped glass (under constant excitation at 292 nm), where that of the blank glass is also given for contrast (colour online)

Another improvement to the current method is its potential to manufacture waveguides with optimized performance. As previously mentioned, the introduction of Ag^+ ions into the glass provides an additional degree of freedom for the regulation and optimization of the waveguide's refractive index profile, thereby enhancing its light-guiding properties. Concurrently, the light-emitting properties can be refined by adjusting the copper doping parameters. Conversely, conventional copper-ion-doped waveguide manufacturing approaches, in which copper ions function as both active and high-polarizability ions, present significant challenges in optimizing light-emitting and light-guiding characteristics concurrently.

It is noteworthy that the presence of copper and silver elements in the glass is contingent on numerous factors, including the doping ion concentration, the composition of the glass material, and the subsequent heat treatment parameters. This is due to the complex reduction-oxidation reaction of copper and silver ions within the glass matrix. In order to leverage copper-ion-doped waveguides in luminescence and nonlinear optical devices, further in-depth studies of the optical waveguide fabrication approach are required.

4. Conclusions

In summary, a two-stage approach to manufacturing a copper-ion-doped channel waveguide on a glass substrate is presented. Subsequent to the doping of copper ions into the surface layer of the glass substrate, the silver ions diffuse into the copper-ion-doped layer, thereby forming the channel waveguide. This approach offers a viable solution for the fabrication of copper-ion-doped channel waveguides through the utilization of melt salt ion exchange. In principle, this approach holds great promise

for the manufacturing of copper-ion-doped functional optical waveguides, which exhibit optimized performance.

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