



Field-driven diffusion of transition metal and rare-earth ions in silicate glasses



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ABSTRACT

The growing applications of glass-based photonic devices, like light waveguides and luminescent materials, demand the development of a versatile diffusion technique. Field-assisted solid-state ion diffusion is a novel technique developed for diffusing transition metal and rare-earth ions in silicate glasses. Due to the limitations of other conventional ion diffusion techniques in the case of multivalent ion diffusion, this technique serves to be equally suitable for the diffusion of both the monovalent and multivalent ions in the glass. In order to understand the mechanism of diffusion, thin films of Au/Er were deposited on soda-lime and borosilicate glass slides, and diffusion was established by applying an external electric field across the sample inside a furnace at a constant temperature. Alkali content of the glass was observed to deplete and the resulting vacancies were filled by the ions from the deposited film. The in-depth diffusion profiles of the doped-glasses were studied using secondary ion mass spectrometry and quantitative analysis was performed with Rutherford backscattering spectrometry. The optical absorption spectroscopy confirmed that the dopants were in non-precipitated form and transmission electron microscopy enabled direct observation of the size and distribution of the doped nanoparticles. The present results demonstrate that the diffusion depends on the processing conditions, glass composition and oxidation rate of the deposited film at the film–glass interface. The observed higher dopant concentration in the soda-lime silicate glass than the borosilicate glass may be due to the higher alkali content in the former glass. The diffusion of considerable amounts of Er content into the superficial layer of the glass, makes it suitable for telecommunication applications.

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1. Introduction

Silicate glasses are doped with transition metal and rare-earth ions to tailor the refractive indices of their superficial layers for specific applications including photonics, glass-based sensors and telecommunication devices [1–6]. A number of different techniques, for example, ion implantation, thermal ion-exchange, sol–gel, sputtering, thermal treatment and melt-quenching have been used to dope these glasses with considerable depths and concentrations, but accompanied by either some limitations or drawbacks [1,7–13]. For example, low penetration depth, inhomogeneous index profile and glass surface damage are among the common drawbacks of ion implantation. In the case of thermal ion-exchange from a salt melt (e.g. AgCl₂), the limited availability of appropriate salts with melting temperatures well below the transition temperature (T_g) of the relevant glass renders it unfeasible. Additionally, this method limits the number of transition metal dopants

to monovalent ions (e.g. Ag⁺) only. In the case of sol–gel technique, the problems associated with making physical electrical contacts with the sol–gel layer(s) limit the field-assisted diffusion. Moreover, in sol–gel-derived Er-doped glasses, the small optical excitation cross-section of Er³⁺ requires a sensitizer to be doped as well. In conclusion, there is a dire need for the development of a new diffusion technique to overcome the abovementioned problems.

In order to extend glass doping from monovalent to multivalent ions and cope with the increasing demand of glass-based components/devices, field-assisted solid-state ion diffusion (FASSID) technique can be a relatively better option [14]. FASSID has been used to dope silicate glasses, and homogeneous and uniform concentration profiles have been reported for both the monovalent and multivalent ions [15–17]. However, the complexity of the diffusion mechanism and involvement of several parameters (e.g. mixed ion-alkali effect [18], non-equilibrium processing and interstitial/defect sites in glass), demand further investigations to assess the suitability of this technique. FASSID may appear similar to thermal poling technique [19] as far as the application of field and heat is concerned; however, the diffusion of dopant ions from an external source only into the superficial layer of the glass

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and internal diffusion of the dopant ions at the cost of alkali ions make it different from thermal poling. Additionally, in FASSID, after the ionic diffusion, no charges or charged poles exist in the doped glass matrix.

This technique has been utilized for the diffusion of transition metals (e.g. Co, Cr, Ag and Au, and rare-earths e.g. Er) in pure silica, soda-lime and borosilicate glasses [16,20,21]. Both the processing temperature and applied electric field play an important role in the diffusion of these dopants; however, the magnitude of the diffusion current across glass matrix depends on the nature of the dopant, oxidation rate of the deposited thin film and host matrix. The doping of high concentrations of optically active Er^{3+} in soda-lime silicate glasses has been confirmed quantitatively by Rutherford backscattering spectrometry and photoluminescence measurements, discussed in detail elsewhere [17]. Er-doping of silica or silica-based matrices has been reported previously using sol-gel derived Er^{3+} -doped silica films [22], radio-frequency co-sputtered Er-doped silica glass films [23], and Er:Ag:Silica atomic beam co-sputtered thin films [24]. Unfortunately, all these conventional ion-exchange techniques are known to have two main limitations i.e. a) after diffusion, the dopants precipitate/cluster together affecting the homogeneity of the doped glass matrix, and b) need a sensitizer to enhance the optical excitation cross-section of Er^{3+} . Thus, the success of FASSID in doping the Er into non-precipitated form and resulting in a high optical excitation cross-section, can be exploited in the development of Er-doped glass-based devices and fibre amplifiers [17,19].

The present study reports preliminary but novel experimental results regarding the diffusion of monovalent as well as multivalent transition metal ions in silicate glasses with considerable concentration. Furthermore, the presence of the non-precipitated form of dopants in the glass matrix allowed post-diffusion treatment to further process the material in a controlled manner for applications in photonics and integrated optoelectronics. A number of characterization techniques e.g. secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), UV-vis spectroscopy and transmission electron microscopy (TEM) were used to investigate the effectiveness of the technique and status of the diffused metal and rare-earth ions.

2. Experimental

Soda-lime and borosilicate glass substrates were cleaned with de-ionized water, trichloroethylene, acetone, and isopropyl alcohol using a five step routine process to ensure good adhesion of metallic layer and avoid any surface contamination. A sodium hydroxide layer was formed on the surface of the glass as a result of reaction in ambient air. This layer lowered the adhesion of metallic film to the glass surface and could be best removed by rinsing with water. The glass slides were heated at 177 °C in a vacuum deposition chamber to redistribute sodium in the matrix, possibly removed from glass surface during cleaning. Thin films (~200 nm) of Au and Er were deposited on commercial soda-lime (SL) and borosilicate (BK7) glasses with atomic % compositions (59.6 O, 23.9 Si, 10.1 Na, 2.6 Mg, 2.4 Ca, 0.7 Mg, 0.5 K, 0.2 S, and traces) and (60.2 O, 22.4 Si, 11.0 B, 3.8 Na, 1.8 K, 0.8 Ba), respectively. About 200 nm thick layers of Ag/Au were deposited on the back of slides as well to make good electrical contact with the negative electrode of the experimental setup. The deposition of these thin films was carried out in a 13.56 Hz radio-frequency magnetron sputtering unit in Ar atmosphere. Additionally, the Er-deposited substrate was heated in an ambient environment for a couple of hours at 350 °C to oxidize the deposited film to form Er_2O_3 . A 200 nm thick Au film was deposited above Er_2O_3 (an insulator) to realize the field-aided diffusion of Er in glass. Edges of the deposited glass slides were properly cleaned to exclude the possibility of direct current flow.

Finally, all the samples were treated in an ambient environment by FASSID technique, inside a furnace at temperatures ranging from 200 to 400 °C in an applied electric field of 100–600 V/mm (Fig. 1). The duration of diffusion was varied from 1 to 4 h and the current through the samples was measured with an interfaced computer. In-depth concentration of the dopant was measured with SIMS by utilizing an IMS-4f Cameca spectrometer. To avoid charge build up on the glass sample, the electron gun was used in normal incidence. A beam of Cs^+ ions with an energy of 14.5 keV is used as incident ions, while secondary ions are detected in an area of $0.125 \times 0.125 \text{ mm}^2$. Quantitative analysis of the

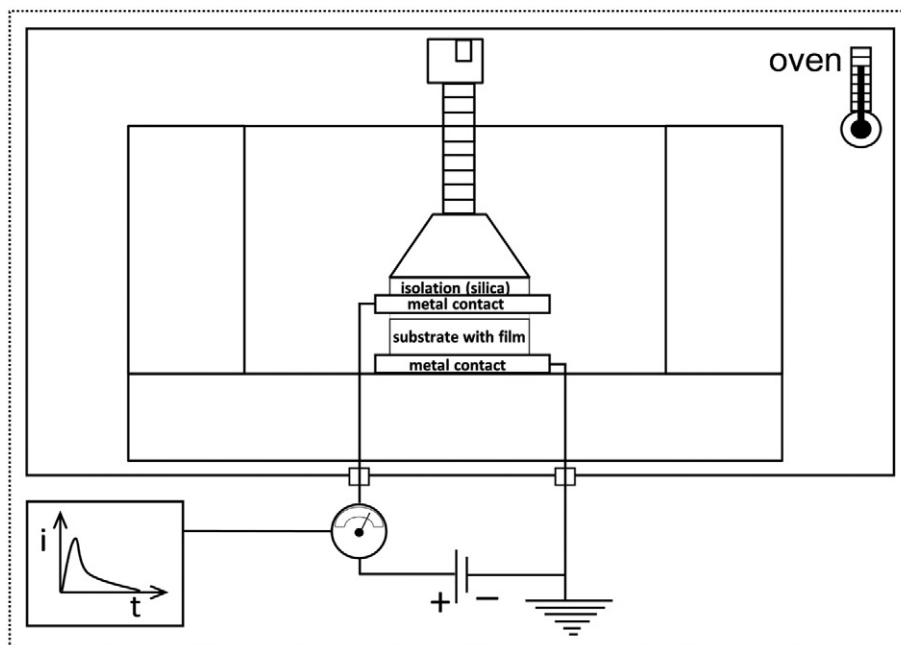


Fig. 1. Field-assisted solid-state ion diffusion experimental setup. Electrical isolation between the electrodes is made by a pure silica slide. A general purpose source-meter supplies voltage and measures current across the substrate, while current vs. time response is plotted on the interfaced computer.

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