Journal of Non-Crystalline Solids 420 (2015) 38–42

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Structural modifications induced in silicate glass by field-aided solid-state diffusion of gold and chromium ions

S. Ali [a], N. Ali [b], Y. Iqbal [a,*], A. Samreen [a], Q. Hayat [b], K. Hayat [a], M. Ajmal [a], M. Javid Iqbal [a]

[a] Materials Research Laboratory, Department of Physics, University of Peshawar, 25120 Peshawar, Pakistan
[b] Department of Physics, Abdul Wali Khan University Mardan, 23200 Mardan, Pakistan

ARTICLE INFO

Article history:
Received 25 February 2015
Received in revised form 8 April 2015
Accepted 10 April 2015
Available online 14 April 2015

Keywords:
Transition metal ions;
Ionic diffusion;
Structural modifications;
Infrared spectroscopy;
Nanoclusters

ABSTRACT

The main objective of this study was to investigate the effect of dopants on the optical properties of sodalime silicate glasses. Consequently, gold and chromium ions were incorporated in the glass matrix via field-aided diffusion for the enhancement of optical properties. The subsequent structural modifications were investigated using secondary ion mass spectrometry, infrared spectroscopy, optical absorption and scanning electron microscopy. Diffusion of Au and Cr ions was carried out at temperatures ranging from 150 °C to 450 °C in an external electric field of strength 100 V/mm to 500 V/mm for 30 to 90 min durations. Diffusion modified the glass structure in the superficial region up to a depth of 1 μm. Analysis of the secondary ion mass spectra revealed uniform diffusion of the dopants and the diameter of the nanoparticles derived from their absorption spectra increased with increasing temperature. The additional bands observed for the doped samples at 1070 cm^{-1}, 1112 cm^{-1} and 1219 cm^{-1} may be due to asymmetric stretching of Si–O–Si induced by Au and Cr diffusion. These structural modifications may be associated with the replacement of the larger host alkali ions ($r_{Na}{}^{+} = 0.99$ Å and $r_{Ca}{}^{+} = 1.0$ Å) with the smaller dopant ions ($r^{3+}_{Au} = 0.85$ Å and $r^{3+}_{Cr} = 0.615$ Å or $r^{6+}_{Cr} = 0.26$ Å). In spite of these structural modifications, the surface of the ion-diffused glass was smooth enough for possible optical applications.

1. Introduction

The growing demand for glass-based new materials has laid the foundation of transition metal ions doped glasses for their potential applications in optics and photonics [1]. The high polarizability of transition metal ions makes them good candidates for laser gain materials, optical waveguides and various other glass-based network components [2]. Consequently, silicate glasses are doped with transition metal ions either by dipping the glass slides in molten salts to exchange the host-alkali ions (mainly Na^{+}) with the dopant ions due to thermochemical potential gradient [3] or from a solid-state metal thin film deposited on the glass surface under an applied electric field at a suitable temperature [4]. In both cases, the diffusion can be considerably controlled by applying an external electric field across the samples subjected to appropriate temperatures.

The refractive index of a silicate glass considerably increases when it is doped with gold and chromium ions, as these dopants possess high polarizability among the transition metals [5]. Au diffusion in sodalime silicate and borosilicate glasses has already been reported for their possible applications in optical waveguides [6,7], surface plasmonics [8], efficient Er^{3+} sensitizers [9] and enhanced photoluminescence [10]. Chromium has been reported to achieve double oxidation states (i.e. Cr^{3+} and Cr^{6+}) when doped into a sodalime silicate glass [6]. In the Cr^{3+} oxidation state, Cr has the potential for applications in photonics, as it is used as laser gain media [11], tunable solid-state lasers [12,13], and as saturable absorbers [14]. Thus, a thorough investigation of ionic diffusion and subsequent modifications in the structure of the doped glass is important for understanding and possible enhancement of the optical properties.

In the present study, field-assisted solid-state ion-diffusion (FASSID) technique was employed to diffuse Au and Cr ions into the superficial layer of the glass by putting the glass slide in between the electrode plates and heated to temperatures well below the relevant glass transition temperature (T_g). A metal oxide layer was formed at the metal–glass interface, and metal ions present in this layer as defects were made to diffuse into the glass matrix by applying an external electric field. The concentration of the diffused metal ions and the subsequent structural modifications in the glass matrix depend on the experimental parameters, the type of dopant and the host glass structure. Here we report results regarding the diffusion of Au and Cr in sodalime silicate glass and the post-diffusion structural modifications induced in the matrix. The diffusion concentration of these dopants was quantitatively assessed by the secondary ion mass spectrometry (SIMS) up to ~3.5 μm in the case of Au and ~1 μm for Cr. The structural modification induced by the dopant diffusion into the glass matrix was studied using Fourier Transformed Infra-Red (FTIR) spectroscopy in the finger print region

---

* Corresponding author.
E-mail address: dryaseeniqbal@yahoo.co.uk (Y. Iqbal).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.04.019
0022-3093/

($400\ \mathrm{cm}^{-1}$ to $1400\ \mathrm{cm}^{-1}$) of the transition metal ions doped silicate glasses. Precipitation of these dopants (especially Cr) depends on the processing conditions and shows plasmonic resonance at 280 nm, as analyzed by the UV–VIS absorption spectrum. Theoretical relations have been formulated to calculate the nano-particle size from the absorption spectra, in agreement with the typical size (~3 nm) of the dopants diffused in silicate glasses by FASSID [15]. The suitability for utilization in various optical applications based on surface morphology was assessed by scanning electron microscopy (SEM).

2. Experimental

Thin metallic films (~200 nm) of Au and Cr were deposited on 1 mm thick sodalime silicate glass slides (atomic % composition: 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 some traces). To make good ohmic contact with the cathode, a metallic silver film (~100 nm) was also deposited on the back side of the sodalime silicate glass slide. The deposition of both Au and Cr was performed by RF-magnetron sputtering deposition apparatus treated with FASSID technique at temperatures ranging from 150 °C to 450 °C, discussed elsewhere [4]. An external electric field (100 V/mm to 500 V/mm) was applied across the samples and the diffusion time was varied from 30 min to 90 min.

To assess depth-wise quantitative diffusion of the dopant, secondary ion mass spectrometry (SIMS) was used to measure the elemental in-depth profiles of chemical species in the deposited film. SIMS measurements were carried out by means of an IMS-4f mass spectrometer (Cameca, Padova, Italy) using a 14.5 keV Cs^+ primary beam and by negative secondary ion detection. The charge build-up during profiling the insulating samples was compensated by an electron gun without any need to cover the surface with a metal film. The SIMS spectra were carried out at 60 nA (stability 0.4%) rastered over $150 \times 150\ \mu\mathrm{m}^2$ area and secondary ion detection from a sub-region close to $10 \times 10\ \mu\mathrm{m}^2$ to avoid crater effects. The primary beam was chosen in order to optimize the depth resolution and multilayer interface determination. The signals were detected in beam blanking mode (i.e. interrupting the sputtering process during magnet stabilization periods) in order to improve the in-depth resolution. Moreover, the dependence of the erosion speed on the matrix composition was taken into account by measuring the erosion speed at two different depths for each sample. The erosion speed was then evaluated by measuring the depth of the erosion crater at the end of each analysis by means of a Tencor Alpha Step profilometer with a maximum uncertainty of a few nanometers. The measurements were performed in High Mass Resolution (HMR) configuration to avoid mass interference artifacts.

Infrared (IR) spectroscopy was used for studying specific molecular vibrations associated with the structural modifications in the superficial layer induced due to the field-aided diffusion of the dopants by using a Thermo Nicolet 6700 IR spectrometer. SEM was performed by INCA 200 annexed with a JEOL JSM-5910 for the analyses of surface features and morphological investigations. The optical absorption of the doped silicate glass was performed using a UV–VIS 1800 Spectrometer in the 200–900 nm range with a step-size of 2 nm.

3. Results and discussions

Fig. 1 shows the SIMS in-depth profiles for Au and Cr doped sodalime silicate glasses, which clearly indicate the yield of dopants and alkali content (mainly Na and Ca). Fig. 1a shows the SIMS in-depth profiles of two Au-doped sodalime silicate glass samples ion-diffused at 450 °C at an applied electric field of 100 V/mm for different durations. To understand the structural modifications and subsequent replacement of the alkali content, one sample was ion-diffused for longer (double processing time) duration than the other. As observed, at a field of 100 V/mm, the depletion of the most mobile Na ions was more evident than the less mobile Ca ions.

Complete depletion of Na ions occurred up to 2 μm in the sample treated for 30 min while an increase in the processing duration was observed to decrease depletion to 1.5 μm. This decrease in depletion depth may be attributed to the simultaneous diffusion of Au into the glass matrix which may have hindered the diffusion. However, in both cases, the depletion of Ca was not much affected by the increase in processing duration and contributed much less to the diffusion of the dopant. The role of the most mobile alkali (Na) ions was clearly evident in the diffusion mechanism and a relatively weaker applied field resulted in a uniform and homogeneous diffusion of multivalent gold (Au^{3+}). This indicated that at a comparatively weaker applied field, the diffusion process occurred almost like a binary ion-exchange. However, the concentration of Au considerably increased (from an average value of 1.8×10^3 counts/s to 5.6×10^3 counts/s) as the diffusion time was increased from 30 min to 60 min. This uniform diffusion (constant rate) after 1.5 μm in both cases indicated a constant injection rate of the dopant and the diffusion process achieved almost an equilibrium state. The observed constancy of the diffusion rate may be attributed to the weaker applied electric field on the multivalent Au^{3+} ions and high temperature across the sample that relaxed the glass structural network for possible replacement of the alkali-depleted sites.

Fig. 1b shows the SIMS in-depth profiles of Cr-doped sodalime silicate glass samples treated at 150 °C to 450 °C at electric fields ranging from 300 V/mm to 500 V/mm for 60 min to 90 min durations. Na was observed to deplete completely up to 1 μm in all the Cr-doped samples

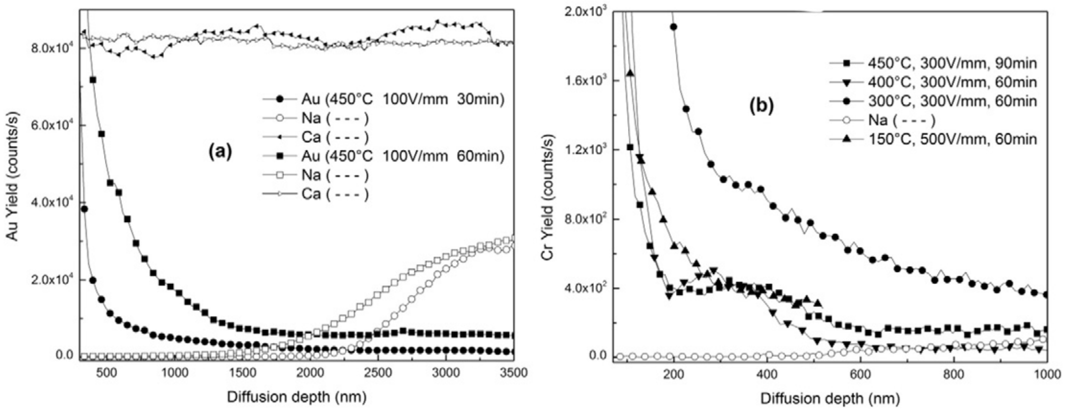

Fig. 1. SIMS in-depth profiles for, a) Au-doped sodalime silicate glasses ion-diffused at 450 °C and 100 V/mm for 30 min and 60 min, respectively, and b) Cr-doped sodalime silicate glass samples treated at 150 °C to 450 °C, 300 V/mm to 500 V/mm, for 60 min to 90 min.