Formation of nanoclusters in silver-doped glasses in wet atmosphere

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Abstract. Thermal stability of silver ions in silicate glasses in dry and wet (0.5- 50% of water content) atmosphere under elevated (160–230°C) temperature is studied. The glass is doped with silver using silver-to-sodium ion exchange procedure conventionally used for the formation of optical waveguides. It is found that the isothermal annealing of glasses doped with Ag⁺ ions in a wet argon atmosphere leads to the reduction of silver to metallic state and to the formation of silver nanoclusters in the glass body. The clustering in the course of water diffusion into the glass was studied by optical spectrometry. The clusters were not formed during annealing in a dry atmosphere at the same temperatures.

1. Introduction
The technique of ion exchange (silver-to-sodium) is used widely for the formation of planar and channel optical waveguides for integrated optics [1, 2, 3], and other GRIN structures [4, 5, 6]. The high polarizability of silver ions, their high diffusivity in the course of ion exchange with sodium, the closeness of ionic radii of silver and sodium, and the existence of proper salts, like silver nitrate and eutectic mixes of other nitrates, allow a wide variety of optical waveguides containing silver ions. The processes of ion-exchange diffusion have been studied and modeled for decades [7- 9], and it is not a difficult challenge to produce an optical waveguide having given parameters in case the glass used for ion exchange is properly characterized. At the same time the studies related to the physics of aging and stability of silver ion-exchanged optical waveguides are rather rare [10- 12]. In this paper we present the results of our studies of the stability of silver ion-exchanged silicate glasses in a wet atmosphere.

2. Experimental
The composition of silica-alkaline glasses melted for the experiments can be presented as the following: (SiO₂)₀.₅(B₂O₃)₀.₁(Al₂O₃)₀.₀₁(Na₂O)₀.₁₆(ZnO)₀.₁₅(ZrO₂)₀.₀₃. The glass was melted at 1550°C with stirring for 2h in a crystabolite crucible. In batch preparation only chemically pure and high-purity grade reagents were used. The melts were poured out into a carbon mould and annealed for 2 h at a temperature corresponding to the glass viscosity equal to about 10¹² Pa·s. The composition of the glass was chosen so as to provide high chemical stability in ion exchange treatment and sufficient index variation. Then a carefully polished glass plate 25x12.5x1 mm³ produced from this glass was subjected to ion exchange processing at eutectic NaNO₃ melt containing 5 mol% of AgNO₃ at 340°C for 4 hours. A planar optical waveguide, formed in this way, was characterized using mode
spectroscopy, and the refractive index profile was found using the White and Heidrich [13] algorithm. The profile is illustrated in figure 1. One can see that maximal variation of refractive index, $\Delta n$, reached at the surface of the sample is 0.0623 and the 1/e depth of the ion-exchanged layer is of order of 20 microns.

![Figure 1. Index profile of the glass sample, after 4h ion exchange processing at 340°C.](image)

Assuming that the index variation is in direct proportion with the concentration of ionic silver [14], this profile allows us to evaluate the depth distribution of silver ions in the samples produced using other ion exchange processing durations, $t$, using the $x \sim t^{1/2}$ dependence, where $x$ is the depth coordinate. For studies of the thermal stability the samples were placed in a furnace, where they were isothermally annealed at a temperature ranging from 160 to 350°C, in flowing argon with various water content that was provided by passing the argon through a water reservoir kept at temperatures between 20 and 93°C, that provided different partial pressure of water vapor. Some of samples were previously annealed in a hydrogen atmosphere to produce a thin (~ 1 μm) layer filled by Ag nanoclusters. Subsequent annealing occurred in a wet Ar atmosphere. After this processing the samples were studied by optical spectroscopy.

3. Results and discussion

Optical absorption spectroscopy demonstrated no changes in the spectra of samples annealed in a dry atmosphere. Since the only possible changes of these samples are related to the redistribution of silver ions in the course of annealing [15], we surmise that dry annealing does not redistribute the ions. All samples annealed in wet atmosphere demonstrated the appearance of new absorption band in the vicinity of 410 nm (figure 2). This absorption peak grew with the increase of humidity, and its position exactly corresponds to the position of the surface plasmon resonance in silver nanoclusters previously observed in silver doped glasses after processing in a reducing atmosphere [16]. Thus this demonstrates that ionic silver is reduced to neutral metal and clustering occurs in silver-rich glasses annealed in a wet atmosphere.

The absorption peak also grows with time if isothermal annealing occurs in a wet atmosphere. At initial stages of annealing optical density grows linearly with $t^{1/2}$ (figure 3). In contrast, annealing in dry argon after annealing in wet argon or in a reducing (hydrogen) atmosphere results in a decrease of the absorption peak.
We suggest that the reduction of silver ions to the metallic state ($\text{Ag}^0$) in a wet atmosphere occurs due to following reactions:

$$\equiv\text{Si}–\text{O}–\text{Ag}^+ + \frac{1}{2}\text{H}_2\text{O} \leftrightarrow \equiv\text{Si}–\text{O}–\text{H}^+ + \frac{1}{2}\text{Ag}_2\text{O}; \quad \text{Ag}_2\text{O} \rightarrow 2\text{Ag}^0 + \text{O}. \quad (1)$$

Silver oxide tends to decompose at elevated temperatures [17], and via partial dissociation of water $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$, which also takes place [18, 19], according to the reaction [20]

$$\equiv\text{Si}–\text{O}–\text{Ag}^+ + \frac{1}{2}\text{H}_2 \rightarrow \equiv\text{Si}–\text{O}–\text{H}^+ + \text{Ag}^0 \quad (2)$$

Here the notifications $\text{Ag}^+$ and $\text{H}^+$ denote ionic bonds silver – oxygen and hydrogen – oxygen, respectively. In spite of a low efficiency of these reactions an accumulation of neutral silver takes place. As the solubility of metallic silver in glasses is negligible, the reduction of silver leads to the oversaturation of the glass, clustering and to the formation of the nanoparticles. The kinetics of clustering caused by reactive hydrogen diffusion were previously analyzed [21], and it was found that the optical density grows linearly with $t^{1/2}$ with practically no change in particle size, whereas the layer filled by the nanoclusters thickens as $t^{1/2}$. According to the analysis, the thickness of the layer filled by nanoclusters, $l$, grows with annealing time as
where \( D_w \) is the water diffusion coefficient, \( N_w \) is the solubility of water molecules in the glass, and \( N_{Ag^+} \) is the silver ion concentration in the doped layer. Then the optical density, \( A(\lambda, t) \), is

\[
A(\lambda, t) \approx 0.43 \cdot \alpha(\lambda) \cdot l(t) \approx 0.61 \cdot \alpha(\lambda) \left( D_w \frac{N_w}{N_{Ag^+}} t \right)^{1/2}.
\]

4. Conclusions
The experiments performed have demonstrated the formation of silver nanoclusters in an alkaline-silica glass subjected to ion exchange after the annealing of the glass samples in a wet atmosphere. The presence of the clusters results from the formation of an optical absorption band specific to surface plasmon resonance of the nanoclusters. The parabolic kinetics of the absorption peak allows us to estimate the product of water diffusion coefficient and water solubility in the glass. The annealing of the glass samples in a dry argon atmosphere does not lead to the formation of the clusters. The results obtained illustrate the possibility of increased optical losses in silver ion-exchanged glass structures due to the effect of humidity at elevated temperatures.

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