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Technical Communication

The development of silver nanoclusters in ion-exchanged soda-lime silicate glasses

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Abstract

Silver-containing soda-lime silicate glasses (chemical composition: 74.2 SiO_2–14.3 Na_2O–1.9 Al_2O_3–8.1 CaO–1.5 MgO, in wt%), formed by ion-exchange process, were thermal annealed in air at temperatures in the range of 500–600 °C. After annealing at 600 °C for 45 h, the spherical nanoclusters were formed with ~3–8 nm distribution in sizes. Increasing the ion-exchanged silver concentration decreased the annealing temperature to form nanoclusters.

Keywords: Glass; Ion exchange; Thermal annealing; Silver nanoclusters

Introducing nanosize metal particles such as silver into glass has been used for changing the color of decorative glasses and recently for fabricating optical devices. Nonlinear optical materials, such as composites formed by metal nanoclusters in glass, are potentially important in the field of optical switching technology [1–4]. Numerous experimental and theoretical approaches have been used to investigate the physical property of metallic nanoclusters in glass have been investigated in the past decades. Extensive studies have been devoted to both the linear and nonlinear properties introduced by optical absorption due to the surface plasmon resonance (SPR). The volume fraction and microstructure of the embedded metal particles, and the dielectric constant of the glass, determine the nonlinear optical properties of these composites.

In the past years, silicate glasses containing silver nanoclusters have been the promising materials for nonlinear optical device fabrication. Ion exchange process with thermal treatment is an important method for obtaining silver nanoclusters in a silicate matrix. Light-ion irradiation and annealing of Ag-exchanged glasses in hydrogen atmosphere (or in a high-vacuum atmosphere) are now widely accepted methods for the preparation of glass materials containing silver nanoclusters, mainly because they are easy to operate and commercially viable for technological applications in optoelectronic devices [4–9]. Although a substantial amount of literature is available on properties of silver nanoclusters in glass which exhibit high optical nonlinear response [10–15], scarcely a little work has been reported on the optical spectroscopic investigations of silver ion-exchanged glass thermally annealing in air. In this paper, we annealed silver ion-exchanged glass in air at higher temperature of 600 °C and longer time up to 45 h. We described the silver nanoclusters formation in commercial flat soda-lime silicate glasses using optical absorption techniques and transmission electron microscope (TEM) measurements in an attempt to understand the formation mechanism during thermal annealing in air, which is the key to optimize thermal processes of glasses.

Commercially available soda-lime silicate glass substrates composed of (wt%): 74.2 SiO_2, 14.3 Na_2O, 1.9 Al_2O_3, 8.1 CaO, and 1.5 MgO were utilized for experimentation. Samples (2 mm thick and of approximately 15 × 15 mm), which had previously been scoured and dried, were preheated and subsequently dipped in a molten salt bath formed by a mixture of 98 mol% $NaNO_3$ and 2 mol% $AgNO_3$ in a crucible of Al_2O_3. The ion exchanges took place at a temperature of 320 °C with a processing time of 10 min or 1 h. To ensure that the glass

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structure did not change during testing, the ion-exchange temperature was kept well below the glass-transition temperature of the specimen. After inter-diffusion, samples were removed from the molten bath and washed with several portions of distilled water and acetone to remove any silver nitrate adhering to their surface.

To promote the silver nanocluster formation, the ion-exchanged samples were thermally annealed in air for 2–45 h at temperatures ranging from 500 to 600 °C. Optical absorption spectra were recorded using a Lambda 9 Perkin-Elmer spectrophotometer at ambient room temperature and all recorded optical spectra were referenced to air. TEM images for representative samples were observed by a TEM (JEOL-2010) at an electron beam energy of 300 keV.

Prior to the ion-exchange process, the glass samples were colorless and had no measurable absorption in the visible region. The soda-lime silicate glasses did not change color after silver exchanging for 10 min. No significant SPR of the silver nanoclusters in glass (400–430 nm) was observed, indicating that the silver aggregate formation did not occur, or the silver nanoclusters were less than 1 nm in size during the 10 min ion exchange. The formation of silver nanoclusters is limited, primarily, to the mobility of silver and the concentration of reducing elements present in the glass. Under our experimental procedures, the silver mobility was minimal and the concentration of reducing agent was relatively low. However, the glass samples showed a slight yellow color after 1 h ion exchange. As the ion-exchange time increased, more diffused Ag^+ could be converted to metallic silver particles by reducing species in glass.

Fig. 1 shows the absorption spectra for silver-exchanged glasses after thermal annealing in air. No obvious absorption band was developed after heating at 550 °C for 2 h. An absorption band at approximately 410 nm was clearly observed after heating at 600 °C for more than 2 h, which was apparently due to the SPR band of silver nanoclusters formed in the glass matrix. When the annealing time increased from 2 to 6 h, a small blue shift of the SPR was observed, indicating that the refractive index property of the matrix or the size of silver nanoclusters was annealing time dependent (Fig. 1(a)). The intensity of absorption at 411 nm increased significantly while the peak position did not change with the increase of annealing time from 6 to 45 h (Fig. 1(b)). The width of the absorption band reduced systematically with the increase of annealing time, indicating an increase of volume fraction of silver nanoclusters in the glass.

From above reported data, the substrate temperature plays a fundamental role in the formation of silver precipitates in Ag-exchanged glass. To form silver nanoclusters in Ag-exchanged glasses with thermal annealing, the temperature was set much lower in reducing atmospheres than in air. When treated in air, nanocluster formation is limited due to low mobility of silver and a lower level of reducing elements present in the glass. Therefore, a higher annealing temperature is desirable [16]. To study the effect of silver diffusion on the formation of nanoclusters, we collected the absorption spectra for samples annealed at 550 °C for 2 h after undergoing 10 min and 1 h ion exchange, as depicted in Fig. 2. Clearly, silver nanoclusters

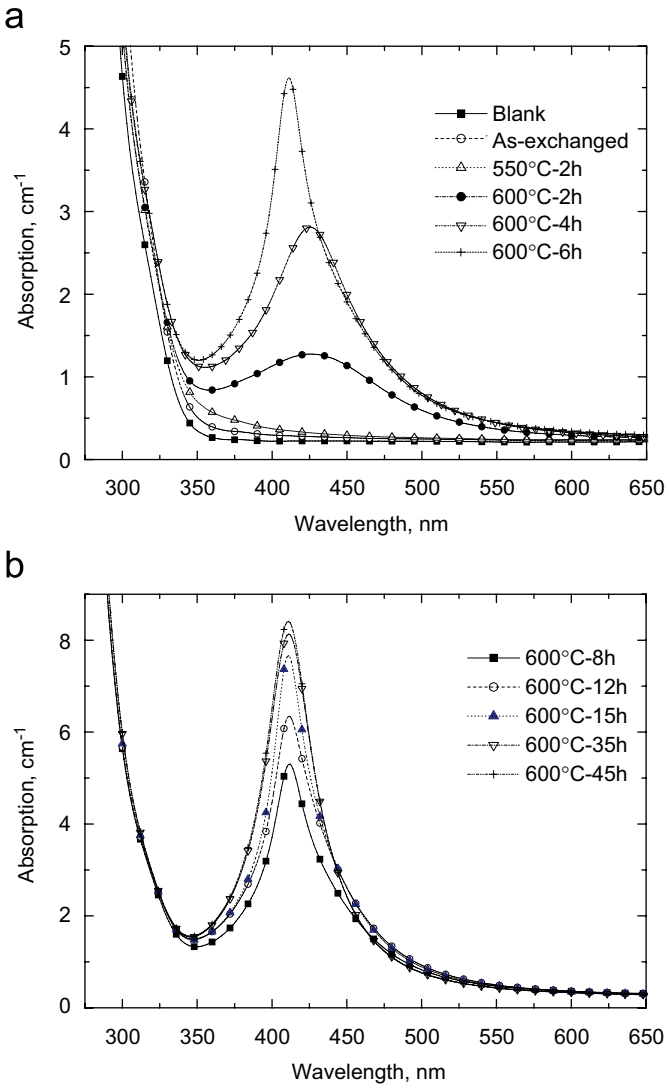

Fig. 1. Optical absorption spectra of silver nanoclusters embedded in 10 min Ag-exchanged glass after thermal annealing.

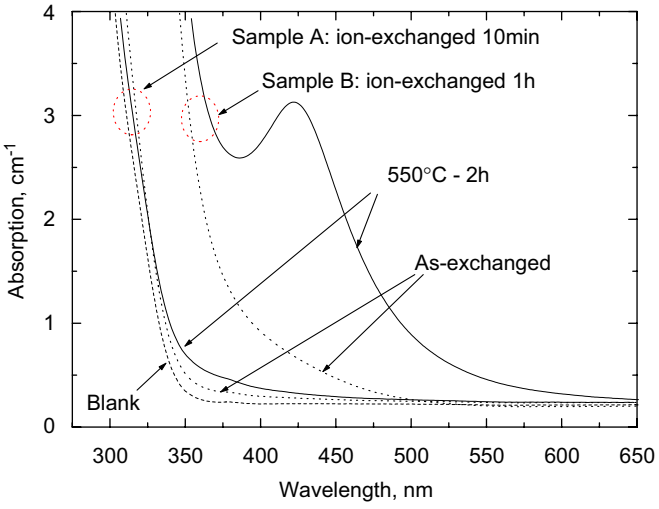

Fig. 2. Optical absorption spectra of silver nanoclusters embedded in 10 min and 1 h Ag-exchanged glasses after thermal annealing at 550 °C for 2 h.