Journal of Non-Crystalline Solids 499 (2018) 278–282

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Electron-beam modification of optical properties of phosphate glasses with high concentration of silver

Alexander I. Sidorov[a,*], Uliana V. Yurina[b], Gulnaz R. Rakhmanova[b], Marina N. Shinkarenko[a], Oleg A. Podsvirov[b], Yuri K. Fedorov[a], Alexey V. Nashchekin[c]

[a] ITMO University, 197101 Saint-Petersburg, Russia
[b] Saint-Petersburg Polytechnical University, 195251 Saint-Petersburg, Russia
[c] Ioffe Institute, 194021 St. Petersburg, Russia

ARTICLE INFO

Keywords:
Phosphate glass
Silver
Molecular cluster
Nanoparticle
Electron irradiation

ABSTRACT

The results of experimental study of silver-containing lanthanum-phosphate glasses, modified by electron irradiation with electrons energy $E = 5$ and 50 keV and thermal treatment are presented. The concentration of Ag_2O in glasses was 17 and 30 mol%. It is shown that initially silver is contained in glasses mainly in a state of subnanosized neutral molecular clusters (MCs). Local electron irradiation results in the increase of MCs concentration in the irradiated zone. This process is accompanied by the appearance of luminescence outside the irradiated zone. Redistribution of silver during electron irradiation is confirmed by X-ray spectral microanalyses. During irradiation with $E = 5$ keV some part of silver migrates to the glass surface, forming the solid silver film. During thermal treatment the growth of silver MCs takes place, and, at last, they form silver nanoparticles (NPs).

1. Introduction

Non-organic glasses, containing noble metals (Ag, Au) or Cu, are polyfunctional optical materials, and are used in photonics and integrated optics. By the external action their optical properties can be modified considerably, also in local regions. For example, in silicate glasses with silver external actions (for example, laser) can produce luminescent silver MCs, luminescent or non-luminescent silver NPs, the change of refractive index, etc. [1–3]. Such glasses possess non-linear optical properties, and are used for volume holograms, optical information and waveguides recording [3–8]. Electron beam processing and subsequent thermal treatment of silver- or copper-containing glasses makes possible to modify their optical properties locally, including nanoscale [9–12]. Electron beam action on alkali or alkali-earth fluoride crystals results in the formation in crystal bulk of corresponding metal nanoparticles even at room temperature [13, 14]. As it was shown in [15, 16] electron beam action on glasses, in some cases, leads to local crystallization of glass. Local electron irradiation of alkali-silicate glasses result in spatial re-distribution of alkali ions [17]. Electron beam action on LiBaAlF6 and LiNbO3 crystals modify their dielectric, optical and luminescent properties [18, 19]. After the electron beam action on lead-silicate glasses their optical non-linearity increases considerably [20]. Electron beam processing of glass and other materials surfaces makes possible on the surfaces metal nanostructures [21–23]. Silicate and phosphate glasses with silver can be also modified by X-rays irradiation [24–26].

The main disadvantage of silicate glasses with silver is that, as a rule, the concentration of silver in them is very low. This is caused by the technological peculiarities of their synthesis. For example, in silicate glasses, described in [1–8], the concentration of Ag_2O was in the range of 0.05–0.12 mol%. In phosphate glasses the concentration of silver can be increased considerably. It gives new abilities for the creation of new functional optical materials. But in most of studies the concentration of silver in phosphate glasses did not exceed several mol. % [24–30]. The goal of the present work was the study of optical properties of phosphate glasses with high concentration of Ag_2O (17 and 30 mol%), locally modified by electron beam.

2. Materials and methods

Lanthanum-phosphate glasses of the system La_2O_3-P_2O_5, doped by Ag_2O with concentrations of 17 mol% (PG17) and of 30 mol% (PG30) were studied. Glasses were synthesized in ITMO University. Glass transition temperatures were measured by differential scanning calorimeter STA 449 F1 Jupiter (NETZSCH-Gerätebau GmbH) and were equal 400–405 °C, depending on glass composition. The samples were

* Corresponding author.
E-mail address: sidorov@oi.ifmo.ru (A.I. Sidorov).

https://doi.org/10.1016/j.jnoncrysol.2018.07.053
Received 9 May 2018; Received in revised form 25 June 2018; Accepted 21 July 2018

prepared as polished plates 10 × 10 mm and 1 mm thick.

For electron irradiation scanning electron microscope JEBD-2 with electrons energy 50 keV was used. Electron irradiation was performed at room temperature. Electron current density was 50 μA/cm^2, and electron irradiation dose was 50 mC/cm^2. Electron beam diameter on the samples surface was 1.5 mm for the convenience of optical measurements. For the deleting of the surface charge, which appears during electron irradiation, Al film 50 nm thick was deposited on samples surface. After irradiation this film was deleted by etching in aqueous solution of KOH. Thermal treatment after irradiation was performed in muffle furnace Nabertherm at 410 °C (higher than glass transition temperature) during 1 h.

Optical density spectra were measure by spectrophotometer Lambda-650 (Perkin Elmer) in spectral range of 300–700 nm. Luminescence spectra were measured by spectrofluorimeter LS-55 (Perkin Elmer) in spectral range of 450–650 nm. Spectral measurements were performed at room temperature. The surface electrical resistance was measured by multimeter HP 3458 A (Hewlett Packard) with the distance between electrodes of 0.8 mm. X-ray spectral microanalyses were performed by energy dispersion spectrometer INCA PentaFETx3 (Oxford Instruments).

3. Experimental results

Electron irradiation with $E = 5$ keV results in the appearance of solid semi-transparent, reflecting silver film on a glass surface (*1* in Fig. 1). Optical density of samples increases up to 0.6 for PG17 and up to 1.3 for PG30 in a wide spectral range (Fig. 2a,b, curves *2*). Minimum at λ = 330 nm corresponds to plasma frequency of electrons in solid silver. The calculation gives the estimation of silver film thickness approximately of 30 nm for PG17 and of 60 nm for PG30. For $E = 50$ keV silver film does not appear on glass surface, but the irradiated zone becomes yellow-brown (*2* in Fig. 1).

For $E = 50$ keV in spectral region from 700 to 320 nm the smooth increase of optical density is observed (curves 3 in Fig. 2a,b). One can see that in the spectrum of PG30 weak absorption bands at 370 and 530 nm appear (curve 3 in Fig. 2b). These absorption bands are caused by the presence of neutral silver MCs in glass (see also below).

Electron irradiation also changes the surface electrical resistance in the irradiated zones. In non-irradiated areas of samples the resistance exceeds 1 GΩ (the measurements limit of the used multimeter). In the irradiated zones for $E = 50$ keV the resistance decreases down to 0.36 GΩ for PG17 and to 0.23 GΩ for PG30. It causes the special interest, because it makes possible to fabricate conducting layers under the glass surface.

Before thermal treatment silver films, formed on the glass surface, were deleted by etching in HNO_3. Thermal treatment of PG17 and PG30 at temperature, higher than glass transition temperature, results in the appearance in optical density spectra of plasmon resonance absorption bands [31, 32] of silver NPs (see Fig. 3). For $E = 5$ keV plasmon resonance absorption bands can be decomposed to two bands with maxima at λ = 390 nm и 420 nm (curves 1 in Fig. 3a,b). For $E = 50$ keV there is one absorption band with maximum at λ = 420 nm (curves 2 in Fig. 3a,b). Plasmon resonance absorption bands in PG30 have larger amplitude than in PG17. It must be noted that in PG30 after

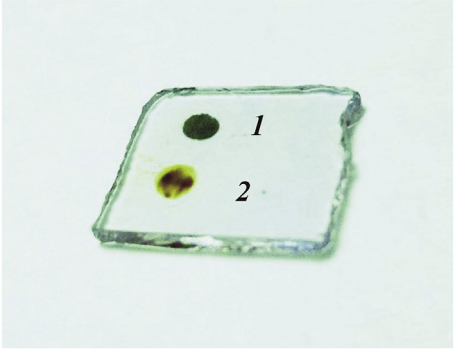

Fig. 1. PG30 after electron irradiation. *1* – $E = 5$ keV, *2* – $E = 50$ keV.

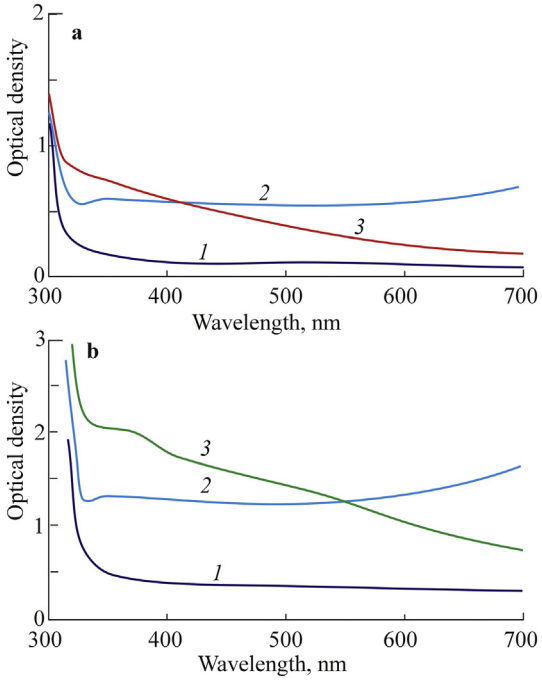

Fig. 2. Optical density spectra of PG17 (a) and PG30 (b). *1* – before electron irradiation; *2,3* – after electron irradiation with $E = 5$ keV (*2*) and 50 keV (*3*).

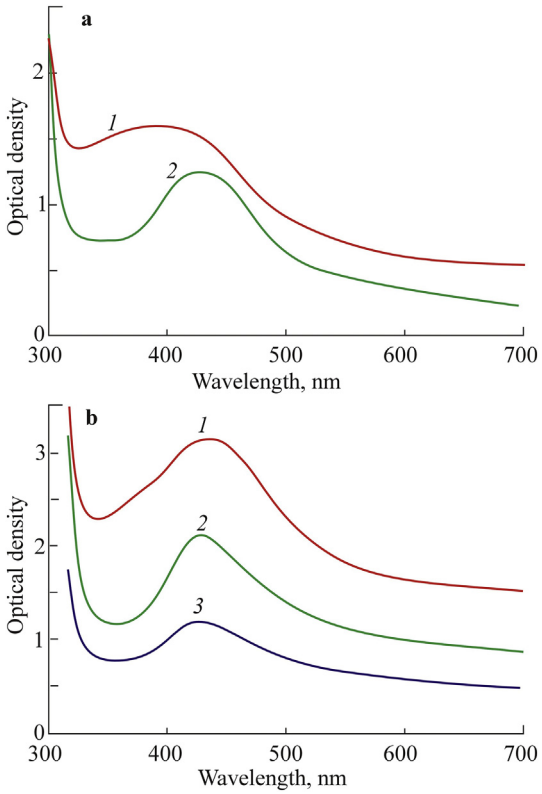

Fig. 3. Optical density spectra of PG17 (a) and PG30 (b) after electron irradiation with $E = 5$ keV (*1*) and 50 keV (*2*) and thermal treatment; *3* – PG30 after thermal treatment without electron irradiation.