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One-step micro-modification of optical properties in silver-doped zinc phosphate glasses by femtosecond direct laser writing

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ABSTRACT

We demonstrate the possibility of joint formation of fluorescent silver clusters and plasmonic silver nanoparticles spatially confined in micron-sized domains by the one-step femtosecond direct laser writing (DLW) without subsequent heat treatment in zinc phosphate glasses with different concentration of silver. We show that DLW in glass induces local micro-modification of optical properties resulted in the appearance of luminescence, absorption and form birefringence in domains. Variation of laser pulse energy allows controlling the micro-modification process and tuning of optical properties. We propose a possible mechanism for observed phenomena that includes local chemical redistribution of glass network modifiers during DLW process. We believe that ability to form complex 3D shapes of luminescent, plasmonic and birefringent structures embedded in dielectric transparent glass materials opens new routes for the design of nanophotonic devices and multi-dimensional optical memory.

1. Introduction

Nowadays nanotechnology represents many ways for processing and tailoring of materials structure at the nanoscale to initiate unique optical properties. One of the significant directions for nanotechnology is development and control of complex metallic nanostructures that can support surface plasmon resonance (SPR) or exhibit fluorescence in particular over large three-dimensionally (3D) areas with high flexibility and speed [1,2]. These nanostructures are of great interest for future applications in nonlinear optics, plasmonic sensing, bioimaging, color displaying and so forth [3]. Despite the advantages of numerous nanolithographic techniques, the 3D manufacturing process is still limited by slow processing speed, complexity in implementation and high production cost.

On the contrary, femtosecond (fs) direct laser writing (DLW) has become a powerful tool for the fast 3D modification of optical materials due to multiphoton absorption of ultrashort pulses [4]. DLW paves the way for the development of composite materials with advanced optical properties and fabrication of functional photonic devices such as integrated waveguides, optical switches, phase plates, 3D optical memory, etc. [5]. Among other materials (polymers, crystals, glass-ceramics) oxide glasses are of particular interest as an object for DLW due to their general availability, low cost, thermal, and chemical stability and excellent optical properties in visible and near-infrared (NIR) ranges that is necessary for the most plasmonic and photonic applications. Along with the properties of glass, parameters of a laser beam applied DLW such as pulse duration, energy and repetition rate play crucial role in the induced material modifications that can give rise to various phenomena such as refractive index change, modification of chemical composition, phase transitions, formation of bubbles or birefringent nanogratings spatially confined in the vicinity of the beam waist [4,5].

Silver and gold nanostructures are among the most promising candidates for future applications in sensing, plasmonics and future optoelectronic integration due to their unique and tunable optical properties: depending on their size they can exhibit intensive fluorescence as nanoclusters (less 1–2 nm in size) or possess well-detectable SPR as nanoparticles (> 3–4 nm in size). Both properties are highly sensitive to size and shape of nanostructures [3,6] and can be tuned in a wide spectral range. However, there are no ways for the further development of complex integrated devices without proper stabilization in dielectric matrix and possibility for precise manipulation of such nanostructures. Thus fs DLW in glasses doped with the noble metal ions offers an opportunity for space-selective generation and stabilization of metal nanostructures in hard dielectric matrix due to series of thermal and chemical processes that take place during DLW [7].

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Phosphate glasses are exceptionally attractive due to their ability to contain photosensitive agents in relatively high concentrations which enables tuning optical properties of the material basing on the wide-range variation of the dopant concentration [8,9]. The interaction of silver-doped phosphate glasses with fs NIR laser pulses during DLW generally can induce space-selective aggregation of fluorescent silver nanoclusters [10,11] or plasmonic silver nanoparticles [12,13]. Additional heat treatment of the glass with locally precipitated fluorescent silver nanoclusters was reported to provide their transformation into plasmonic silver nanoparticles [7]. Formation of these metal nanostructures takes place in the edges of 3D spatially confined pipe-shape domains elongated along the laser beam. Ability to form fluorescent nanoclusters and plasmonic nanoparticles by the one-step DLW process is a perspective way for a wide range of applications in sensing, nonlinear and plasmonic integrated devices, multidimensional optical memory, etc. Recently we briefly reported the possibility of luminescent and birefringent domain formation during DLW in the phosphate glass [14]. However, to the best of our knowledge, no studies of the simultaneous laser-induced formation of fluorescent and plasmonic silver nanoparticles in glass originating from fs DLW have been conducted so far. It is worth noting that most of abovementioned studies were performed on glasses melted in platinum crucibles that exclude the possibility of any impurities addition such aluminum oxide which can strongly influence on the changes in the glass structure [15,16].

Herein we report the possibility of simultaneous formation of fluorescent and plasmonic silver nanostructures by the one-step fs DLW without subsequent heat treatment in zinc phosphate glasses with different content of silver melted in corundum crucibles. Moreover, we show that laser-induced domains exhibit birefringence at the periphery of the laser-induced domains correlated with precipitation of plasmonic silver nanoparticles.

2. Experimental

2.1. Glass preparation

Glasses with molar composition $xAg_2O - (100-x) \cdot [57ZnO - 43P_2O_5]$(x = 0,1,4,8,16 mol%) were prepared by a conventional melt-quenching method. The corresponding glasses are further referred to as PZA, PZA-1, 4, 8, 16, respectively (Table 1). High-purity raw materials: H_3PO_4, ZnO and $AgNO_3$, were mixed and the liquid batch was portionwise poured into a corundum crucible placed in a furnace at 275 °C. After that the crucible was covered with a corundum cap to reduce evaporation during melting. The melting was performed in an electrically heated furnace at 1200 °C for 2 h. Since these melts were very fluid, homogenization occurred by convection without stirring. After casting the melt into a steel mold, the glass was annealed at 300 °C for 4 h. Samples were polished to optical quality. Only strain- and bubble-free glasses were used for subsequent experiments.

2.2. Femtosecond direct laser writing

The DLW experiments were conducted using a Pharos SP laser (Light Conversion Ltd) with 1030 nm central wavelength, max pulse energy of 0.8 mJ and mean power up to 6 W. The laser was tuned to 100 kHz pulse repetition rate and 600 fs pulse duration. The glass sample was placed on XYZ-motorized air-bearing ABL1000 stage (Aerotech). The laser beam was focused inside the sample using microscope objective (40 ×, NA = 0.55, Olympus) at a depth of 100 μm. The glass was exposed to laser pulses with different energy in the range from 18 to 144 nJ and different number of pulses from $1{,}25 \cdot 10^5$ to 10^6. Three orientations of the laser beam polarization plane rotated by 0, 45 and 90° relative to the starting orientation using a half-wave plate were applied during laser writing of domains for each pulse energy value and number of pulses. To measure the absorption and emission spectrum of the glass sample after the DLW, a 5.0 × 5.0 mm square consisting of parallel tracks laser-written with a step of 5 μm.

Table 1
PZA glass compositions and properties.

Sample label	Composition, mol.%			Tg, °C (± 2)	Density, g/cm^3 (± 0.01)
	Ag_2O	ZnO	P_2O5		
PZA	–	57,3	42,7	425	3,13
PZA-1	1	56,7	42,3	402	3,20
PZA-4	4	55,0	41,0	371	3,37
PZA-8	8	52,7	39,3	362	3,61
PZA-16	16	47,9	36,1	357	3,89

2.3. Glass characterization

The glass transition temperature (Tg) of the glasses under study was determined by differential scanning calorimetry (DSC) for the bulk samples using a STA 449 F3 Jupiter (NETZSCH) analyzer at a heating rate of 10 °C/min; measurement error was ± 2 °C and was related to the instrumental error. Density of the samples was measured by hydrostatic weighing, measurement error was ± 0.01 g/cm^3 and was derived as mean average deviation between three measurements. The surface crystallization of the glasses was analyzed by means of D2 Phaser diffractometer (Bruker). Absorption spectra of bulk samples were recorded using UV-3600 spectrophotometer (Shimadzu). Absorption and emission spectra of a laser-modified area inside the glass were measured using a micro-spectrophotometer based on MS3504i monochromator (SOL instruments Ltd) combined with Olympus BX51 optical microscope. Fluorescence and transmission optical images of the laser-exposed regions were obtained with a confocal fluorescence microscope Olympus BX41TF (excitation at 340–380 nm, emission at 430–480 nm). The laser-induced birefringence was characterized by retardance and slow axis orientation which were measured and visualized with the quantitative birefringence measurement system Abrio Microbirefringence (CRi) installed in Olympus BX51 microscope and operating at 546 nm. Error bars for the measured retardance values were derived as a mean average deviation of the retardance in ten domains written with 10^6 laser pulses with the pulse energy of 54 nJ. A detailed analysis of nanoparticles precipitated in the edges of ring-shaped domains was performed by means of transmission electron microscopy (TEM) using Titan 80-300 S/TEM system (FEI, USA). TEM images received in 300 kV mode also by using of STEM bright-field (BF) and high-angle annular dark-field (HAADF) detectors. No effect of electron irradiation on the nanostructured domains was observed during measurements. A cross-section slice of the domain was prepared as a specimen for TEM analysis by ion beam etching. The local elemental analysis was performed by Energy-dispersive X-ray spectroscopy (EDS) combined with Titan 80-300 S/TEM system.

3. Results

3.1. Properties of the pristine glass: the influence of silver

Increase of silver oxide content in the studied glasses from 0 to 16 mol% leads to notable changes in their properties (Table 1, Fig. 1) decreasing their glass transition temperature (Tg) from 425 to 360 °C (Fig. S1) and increasing their density from 3,13 to 3,89 g/cm^3 while changing silver oxide content from 0 to 16 mol%. Optical absorption spectra of the glasses don't show any noticeable absorption in the visible range (Fig. 1). Heat treatment of silver-doped glasses in the temperature range below and above Tg (340–450 °C) for 2 h didn't give rise to any changes in optical absorption spectra (Fig. S2). It should be noted that absorption spectra of the heat-treated samples were measured after additional surface polishing. The glasses exhibit strong