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Femtosecond laser processing of Ag/CdS doped oxide glasses

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ABSTRACT

Femtosecond laser processing (FLP) of oxide glasses doped with photosensitive agents (noble metals and semiconductors) opens new routes for precise space-selective tuning of material properties and development of functional photonic devices including integrated waveguides, optical switches, and volume optical memory. In this study, we showed how FLP can be used for the spatially-selective formation of micron-sized photoluminescent domains in the bulk of Ag-doped phosphate and Ag/CdS-doped silicate glasses. Multiphoton ionization caused by FLP leads to local heating of glass in the focal point, which initiates the precipitation and growth of photoluminescent Ag nanoclusters and CdS quantum dots in the periphery of the domains. The photoluminescence intensity of the formed domains depends on the laser exposure parameters, such as pulse energy and number of pulses that can be used in the future for multilevel optical data recording.

1. INTRODUCTION

Glasses with noble metals and chalcogenide semiconductors are popular subject of numerous studies for applications in optics and photonics [1-4]. The main feature of these glasses is possibility of bulk precipitation of metal or semiconductor nanoparticles with different sizes which could dramatically change the optical properties of glass. It is possible to control size of nanoparticles both by varying dopant concentration and heat-treatment conditions i.e. temperature or duration.

In recent decades availability of high powered femtosecond lasers created new type of studies related to the laser processing of optically transparent materials (crystals, glasses, films, etc.) [5] for space-selective structure modification and fine tuning of its properties. This method known as a direct laser writing or femtosecond laser processing (FLP). FLP of glasses with particular chemical composition is known to make it possible to write, erase and rewrite various micro- [6, 7] and nanostructures [8] in the glass volume. At the same time, variation of laser parameters opens ways to control the optical characteristics of the laser-written domains. In particular, the possibility of space-selective precipitation of Ag and CdS nanoparticles in the bulk of oxide glasses by femtosecond laser beam is promising for the fabrication of miniature optical components for nanophotonics, photovoltaics, optoelectronics, and data storage [9, 10].

Recently, one-step precipitation of silver nanoclusters and nanoparticles in phosphate glass under the femtosecond laser beam has been demonstrated [11]. The laser-induced domains have a yellow coloration and show tendency to photoluminescence and birefringence, the latter being dependent on the polarization of the writing laser beam. Similar studies on the formation of metal nanoparticles or semiconductor quantum dots were also carried out for silicate glasses [12, 13]. However, additional heat treatment of laser-modified glasses is generally required to precipitate and grow nanoparticles. It was shown [12] that only Ag^+ ions are formed in a femtosecond laser-modified area. Additional heat treatment induces

aggregation processes which lead to an increase of photoluminescence intensity [13]. The similar behaviour is observed for laser processing of semiconductor-doped glass. Colourless and nonluminescent domains are formed after laser exposure of glasses but the following heat treatment of laser-written domains induces their photoluminescence due to the nanoparticle formation [14, 15]. The proposed technique allows precipitation of semiconductor nanoparticles in glass bulk, but its efficiency is poor due to the necessity of long-term heat treatment of laser-exposed glass.

Recently, our group has shown a possibility of direct laser-induced precipitation of CdS quantum dots in the bulk of silicate K_2O-ZnO-B_2O_3-SiO_2 glass [16]. In this regard, it is important to continue the investigation of the one-step precipitation of silver nanoclusters and nanoparticles under a femtosecond laser beam in the same glass host. Thus, this research is devoted to investigation and comparison of optical features of the domains laser-written in silicate and phosphate glasses doped with Ag and CdS.

2. EXPERIMENTAL

In this work, we synthetized silicate glass in the K_2O-ZnO-B_2O_3-SiO_2 system, concentration of silver was 0,1 wt.% (further marked as OS-0.1Ag) and that of CdS was 1 wt.% (OS-1CdS). Glass without dopants marked as OS was also synthesized. The batch was loaded into a corundum crucible at 1100°C. Glass melting was carried out in a laboratory electrical furnace at 1270°C for 1 h. To minimize volatilization of glass components, the crucible was covered with a fused silica cap. Resulting glass melt was poured into preheated to 500°C steel mould to prevent crackling of glass. Annealing of glass cast was performed in a muffle furnace at 500°C for 4 h with subsequent slow cooling to the room temperature. Also we investigated zinc phosphate glass in the Ag_2O-ZnO-P_2O_5 with 8 mol.% of Ag_2O marked as PZA-8, synthetized by the similar methodology.

Glass samples of 10x10x3 mm^3 size were polished into plane-parallel plates for direct laser writing process. In our work, we used an experimental setup based on Pharos SP femtosecond laser system with 1030±2 nm central wavelength which was tuned to 100 kHz pulse repetition rate and pulse duration of 180 fs. Pulse energy was varied in the range 100-400 nJ and each domain was written by a number of laser pulses varying from 10^1 to 10^6. The laser beam was focused into the glass sample by an Olympus microscope objective (20X, N.A.=0.45) at the depth of ~150 μm under the surface. The glass sample was moved by means of a three-coordinate motorized air-bearing translation stage (Aerotech ABL1000) synchronized with the laser.

Optical characterization of the laser-written domains was performed using an Olympus BX41TF luminescence microscope equipped with a DP73 CCD camera. The photoluminescence excitation was provided by the mercury lamp and the Olympus U-MNV2 photoluminescence cube was used to separate emitted light from excitation one. Obtained optical and photoluminescence images of the written domains were analysed by means of ImageJ software. Study of cross-section slice of the domain written in PZA-8 glass sample was performed by transmission electron microscopy (TEM) using Titan 80-300 system (FEI, USA); the local elemental analysis was performed by energy-dispersive X-ray spectroscopy (EDS) combined with Titan 80-300 system.

3. RESULTS AND DISCUSSION

Set of ring-shaped domains was written in prepared glass samples by the focused femtosecond laser beam (Fig. 1). When a sample of OS-1CdS glass is exposed to 10^6 laser pulses with energy over 300 nJ a strong yellow coloration is observed in the periphery of the domains, which may be caused by the precipitation of CdS nanoparticles in that area. At the same time, no coloration was observed for domains in OS-0.1Ag glass even at maximum values of pulse energy and number of pulses (Fig 1a). Increasing pulse energy from 100 to 400 nJ at 10^6 pulses per dot resulted in an increase of the linear dimensions of the domains from 4.5 to 9.5 μm and from 4.5 to 12 μm for OS-0.1Ag glass and OS-1CdS glass, respectively. Thus, a variation of the pulse energy is an effective laser exposure parameter to control the size of the laser-written domains. Luminescence microscopy images (Fig. 1b) evidently show the

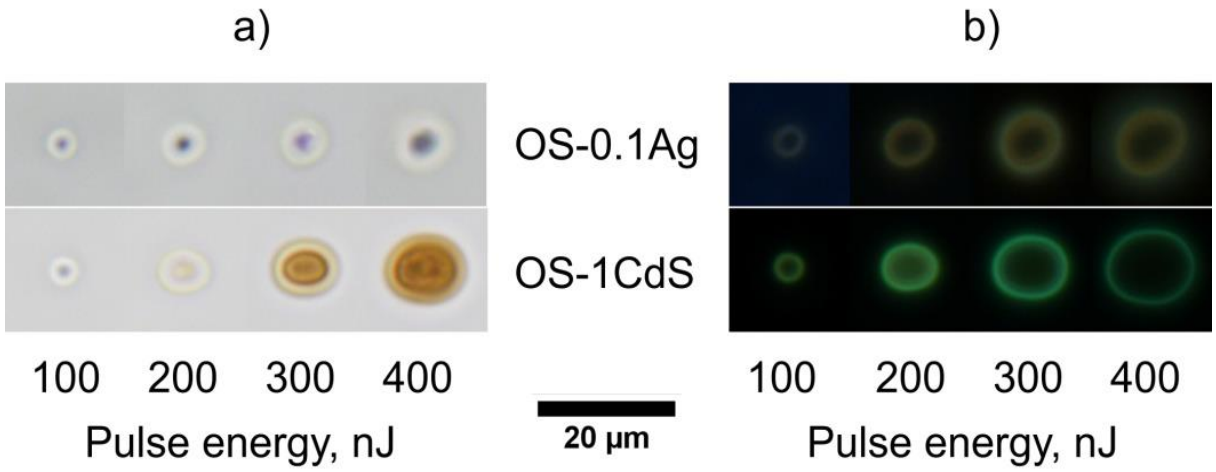

Figure 1. Optical (a) and photoluminescence (b) images of ring-shaped domains laser-written in OS-0.1Ag and OS-1CdS glass samples with different pulse energy from 100 to 400 nJ at 10^6 pulses. Luminescence excitation wavelengths – 400-410 nm, registration wavelengths – 455-800 nm.

photoluminescence occurrence on the periphery of the written domains. It should be mentioned that FLP of OS glass sample free of Ag or CdS also lead to the formation of ring-shaped domains while no coloration or photoluminescence was observed for this sample. It is also known that laser irradiation of glasses can induce the formation of radiation defects which caused yellowish to reddish coloration of glass and may be misinterpreted as nanoparticle precipitation [17]. These radiation defects are thermally unstable and degrade after being heated up to 200-300°C. To confirm Ag or CdS precipitation and exclude a possible factor of radiation defects we performed a thermal treatment of both OS-0.1Ag and OS-1CdS laser-exposed glass samples at 350°C for 1 h. No degradation of photoluminescence from the laser-written domains was observed after the heat treatment.

A numerical analysis of photoluminescence intensity from the written domains showed that for

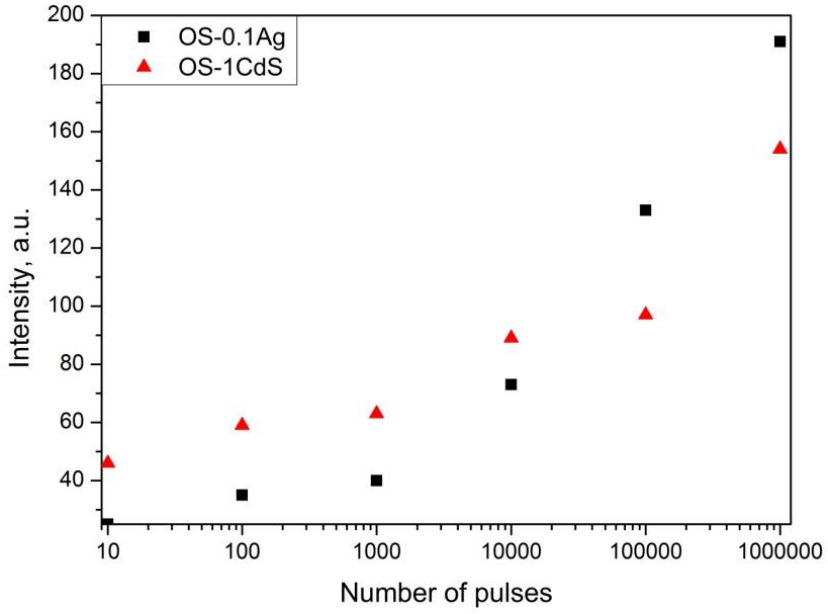

Figure 2. Luminescence intensity of written domains dependence on the number of laser pulses at 400 nJ pulse energy.

both studied glasses an increase in pulse energy up to 200 nJ leads to the formation of domains with maximum photoluminescence intensity. Importantly, the observed photoluminescence (Fig. 1b) lets us assert the formation of small nanoparticles of CdS and silver nanoclusters in the laser-written domains. The further increase in pulse energy resulted in photoluminescence quenching that can be related to the formation of large CdS particles in OS-1CdS glass and the beginning of the processes of aggregation of silver nanoclusters into larger agglomerates in OS-0.1Ag glass. It should be noted that simultaneous formation of both small and large nanoaggregates generally occurs in laser-written domain due to Gaussian energy distribution in the laser beam and corresponding temperature profile.

We also performed an analysis of photoluminescence intensity evolution with a number of writing laser pulses for domains written with 10^1 to 10^6 pulses at 400 nJ pulse energy (Fig. 2). One can see that the larger number of pulses, the higher photoluminescence intensity. The rate of the increase in the photoluminescence intensity is lower for OS-1CdS glass than for OS-0.1Ag glass when number of pulses is 10^4-10^6. This phenomenon can also be tentatively explained by the formation of large nanoparticles of CdS causing quenching of photoluminescence from smaller particles.

When comparing the results obtained for glasses OS-0.1Ag and OS-1CdS, it is important to take into account the concentration of the dopant. In this work, the concentration of silver in glass OS-0.1Ag was 10 times lower than the concentration of CdS in glass OS-1CdS, but when comparing the photoluminescence intensities of the written domains, we obtained relatively similar results. Thus the determination of the optimal concentration of particular dopant in glass is required for achieving the maximum photoluminescence intensity of the written domains. This determination will be done by studying silicate glasses with different concentrations of photosensitive dopants. Also by varying the parameters of FLP (pulse energy and number of pulses) it is possible to record data in the photoluminescence intensity signal of written domains in several levels of intensity which is open

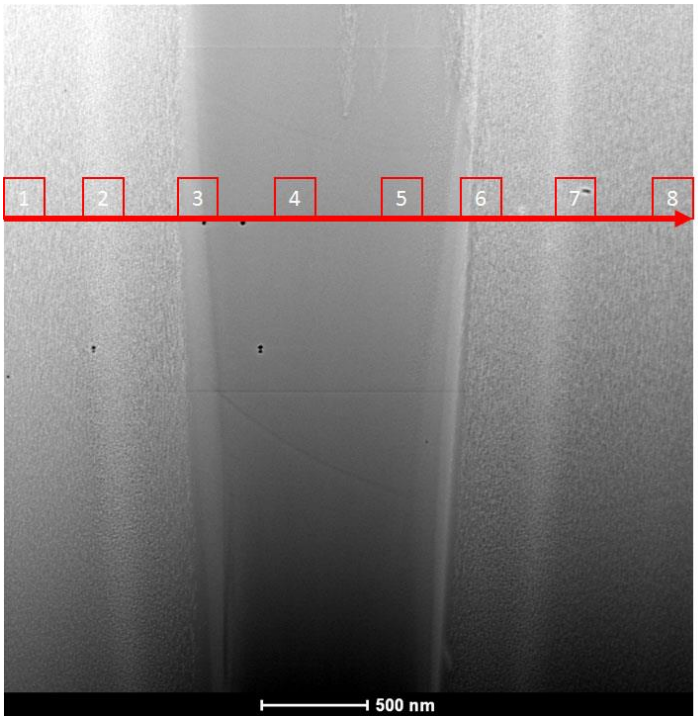

Figure 3. TEM image of cross-cut form the domain laser written in PZA-8 glass sample. Direction of laser beam: up-down. Red arrow shows direction of EDS scan; numbers refer to EDS measurements on Fig. 4.

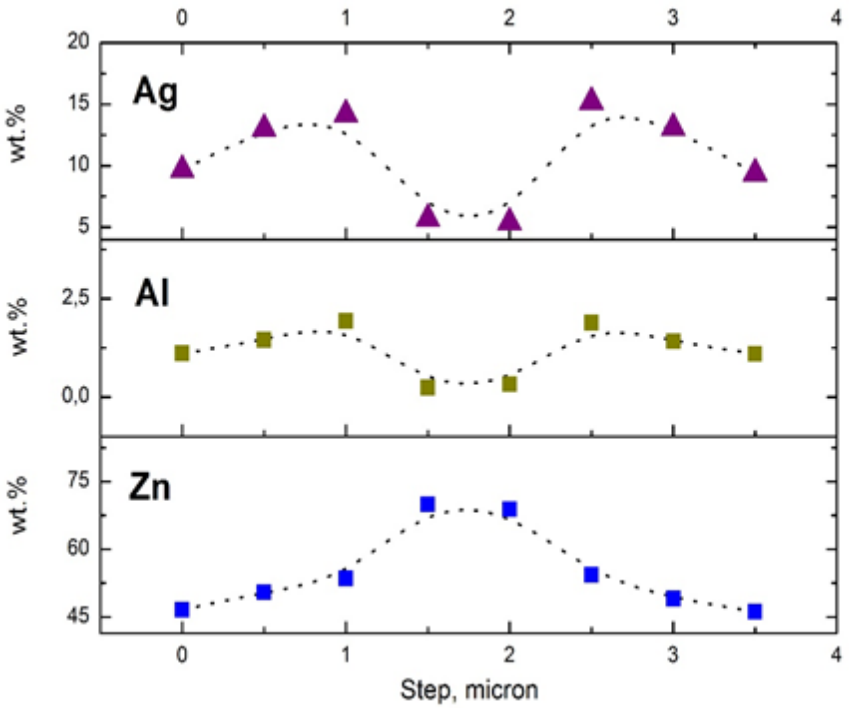

Figure 4. Results of local EDS measurements of cross-section from Fig.3.

routes for multilevel data recording in the bulk of robust and chemically stable silicate glass.

In recent works [11, 18, 19] we studied formation of silver particles (both clusters and plasmonic nanoparticles) in zinc phosphate glasses referred as PZA. We showed that by tuning FLP parameters it is possible to locally precipitate Ag nanoparticles in glass. In this work by means of TEM and EDS we studied phenomenon of local ions migration during FLP.

Fig.3 shows TEM image of cross-cut obtained by ion beam etching of domain laser written in PZA-8 glass sample at 100 nJ and 10^6 laser pulses. Since glass network formers have a stronger binding energy with oxygen than the network modifiers, they tend to remain at the center of the domain's area. Thus FLP of glasses doped with noble metal ions (Au, Ag) that always act as network modifiers, leads to the precipitation of metal nanoparticles and formation of structures with unique optical properties such as surface plasmon resonance or photoluminescence. In all previous studies concerning silver or gold doped glasses, thermal treatment near the glass transition temperature was reported to induce homogeneous volume precipitation of metal nanoparticles inside the glass [20-23]. Generally, this originates from the reducing of Ag/Au ions to neutral atoms with the help of reducing agents (SnO_2). Neutral metal atoms tend to agglomerate within the formation of metal nanoparticles. In our case we performed one-step precipitation of silver clusters and nanoparticles that is confirmed by TEM revealing chemical contrast in central and side areas of cross-cut. This difference gives preliminary insights in the spatially-selective ion migration process occurred during the FLP of glass.

In order to confirm ion migration in phosphate glass we performed EDS measurements in eight points along cross-section according to Fig.3. Fig. 4 shows results of EDS measurements. One can see that silver concentration is slightly higher in periphery areas and lower in central area. Same effect can be seen for aluminium ions which were introduced in glass during melting in corundum crucible. On the other hand, zinc concentration increased is central area that is typical for network former components.

Comparing results for FLP of silicate and phosphate glasses one can see significant

similarities that are expressed in local changes of chemical composition and element redistribution. Both type of glasses poses photoluminescence on the edges of laser written domains due to precipitation of Ag clusters or CdS quantum dots. At once structural peculiarities of phosphate network allow to obtain glasses with much larger content of silver comparing to silicate glass.

4. CONCLUSIONS

We showed that FLP is a useful technique for one-step spatially-selective formation of micron-sized photoluminescent domains in the bulk of Ag- and CdS-doped glasses by the example of silicate and phosphate glasses. It was demonstrated that the precipitation and growth of photoluminescent Ag nanoclusters and CdS quantum dots occur in the periphery of laser-written domains. We managed to control the size and optical characteristics of laser-written domains by varying pulse energy and number of pulses. Also, we confirmed occurrence of ion migration process in silver doped zinc phosphate glass. FLP of glass leads to migration of glass network modifiers (such silver) to the periphery of written domains, while migrations of network formers direct to the central area of domains. Obtained results give important information about possibilities of local chemical change and open a prospect of FLP for application in multilevel optical data storage and optical waveguides.

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