Femtosecond direct laser writing in silicate glasses doped with silver and cadmium sulfide

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Abstract. Femtosecond direct laser writing (DLW) in 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 DLW can be used for the spatially-selective formation of micron-sized luminescent domains in the bulk of Ag-doped and CdS-doped silicate glasses. Multiphoton ionization caused by DLW leads to local heating of glass in the focal point, which initiates the precipitation and growth of luminescent Ag nanoclusters and CdS quantum dots in the periphery of the domains. The luminescence 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 doped with noble metals and chalcogenide semiconductors have been the subject of numerous studies for applications in optics and photonics [1-4]. A distinctive feature of these glasses is the possibility of bulk precipitation of metal or semiconductor nanoparticles with different sizes, which could dramatically change the optical properties of the bulk material. The size of nanoparticles can be controlled by varying the dopant concentration and heat-treatment conditions, i.e., temperature or duration. Nowadays, there are many studies related to the space-selective modification of the structure of optically transparent media (crystals, glasses, films, etc.) by a femtosecond laser beam known as direct laser writing (DLW). DLW in glasses with a particular chemical composition is known to allow writing, erasing and rewriting various micro [5, 6] and nanostructures [7] in the glass bulk. At the same time, varying the parameters of DLW provides a way 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 a femtosecond laser beam is promising for the fabrication of miniature optical components for nanophotonics, photovoltaics, optoelectronics, and data storage [8].

Recently, one-step precipitation of silver nanoclusters and nanoparticles has been demonstrated in phosphate glass under the femtosecond laser beam [9]. The laser-induced domains have a yellow coloration and show a tendency to luminescence 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 [10, 11]. However, the precipitation and growth of nanoparticles generally require additional heat treatment of laser-modified glasses. Miyamoto et al. [10] showed that only Ag$^{+}$ ions are formed in the area modified by a femtosecond laser. Additional heat treatment induces aggregation processes, which lead to an increase in the luminescence intensity [11]. Similar behavior is observed for DLW in semiconductor-doped glass. Colorless and nonluminescent domains are formed after laser exposure of glasses, but the following heat treatment of laser-written domains enhances their luminescence efficiency due to the nanoparticle formation. The proposed technique allows precipitation of semiconductor nanoparticles in the glass bulk, but its efficiency is poor due to the necessity of long-term heat treatment of the laser-exposed glass.

Recently, our group has demonstrated the possibility of direct laser-induced precipitation of CdS quantum dots in the bulk of silicate K$_2$O-ZnO-B$_2$O$_3$-SiO$_2$ glass [12]. In this regard, it is important to continue the investigation of the one-step precipitation of silver nanoclusters and nanoparticles under the influence of a femtosecond laser beam in the same host glass. Thus, this research is devoted to the investigation and comparison of the optical features of laser-written domains in K$_2$O-ZnO-B$_2$O$_3$-SiO$_2$ glasses doped with Ag and CdS.

2. Experimental

In this work, we used K$_2$O-ZnO-B$_2$O$_3$-SiO$_2$ glass as a matrix, which is typical for industrial manufacturing of color glass filters. High purity grade reagents (SiO$_2$, H$_3$BO$_3$, ZnO, K$_2$CO$_3$, CdS, AgNO$_3$) were thoroughly mixed to obtain a homogeneous batch. The concentrations of silver were 0.1, 0.5, and 1 wt.% (further denoted as OS-0.1Ag, OS-0.5Ag and OS-1Ag, respectively) and CdS was 1 wt.% (named as OS-1CdS). Glass without dopants, denoted as OS, was also synthesized. The batch was loaded into a corundum crucible at 1100°C. Glass was melted 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. The resulting glass melt was poured into a steel mold preheated to 500°C to prevent the glass from cracking. The glass cast was annealed in a muffle furnace at 500°C for 4 h and then slowly cooled to room temperature.

![Figure 1](image.png)

**Figure 1.** Diagram of the experimental setup for the DLW.

Glass samples of 10 x 10 x 3 mm size were polished into plane-parallel plates for direct laser writing. In our work, we used an experimental setup (figure 1) based on the Pharos SP femtosecond laser system with a central wavelength of 1030 ± 2 nm, which was tuned to a pulse repetition rate of 100 kHz and a pulse duration of 180 fs. The 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 a 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 luminescence excitation was provided by a mercury lamp, and the Olympus U-M NV2 luminescence cube was used to separate the emitted light from the excitation one. The obtained optical and luminescence images of the written domains were analyzed using ImageJ software.

3. Results and discussion

Initial glasses doped with 0.5 and 1% of silver were opaque, likely due to a high concentration of silver which was not completely dissolved in the glass bulk during the glass melting process. Due to this fact, the samples of these glasses were not used in laser writing experiments. On the contrary, the OS-0.1Ag and OS-1CdS glasses were colorless, transparent, and suitable for femtosecond laser modification.

A set of ring-shaped domains was written in the prepared glass samples by a focused femtosecond laser beam (figure 2). When a sample of OS-1CdS glass is exposed to 10^6 laser pulses with an energy of more than 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 is observed for domains in OS-0.1Ag glass even at the maximal applied values of the pulse energy and number of pulses (figure 2(a)). Increasing pulse energy from 100 to 400 nJ at 10^6 pulses per dot resulted in an increase in 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, variation of the pulse energy is an effective laser exposure parameter to control the size of the laser-written domains. Microscope luminescence images (figure 2(b)) clearly show the occurrence of luminescence on the periphery of written domains. It should be mentioned that DLW in the OS glass sample free of Ag or CdS also leads to the formation of ring-shaped domains while no coloration or luminescence was observed for this sample. It is also known that laser irradiation of glasses can induce the formation of radiation defects, which cause a yellowish to reddish coloration of the glass and may be misinterpreted as the nanoparticle precipitation [13]. These radiation defects are thermally unstable and degrade after being heated up to 200 - 300°C. To confirm the Ag or CdS precipitation and exclude the possible factor of radiation defects, we thermally treated both OS-0.1Ag and OS-1CdS laser-exposed glass samples at 350°C for 1 h. No degradation of luminescence from the laser-written domains was observed after heat treatment.

![Figure 2](image_url)

**Figure 2.** Optical (a) and luminescence (b) images of ring-shaped domains laser-written in OS-0.1Ag and OS-1CdS glass samples with varying pulse energy from 100 to 400 nJ at 10^6 pulses. The luminescence excitation wavelengths are 400 - 410 nm; the registration wavelengths are 470 - 800 nm.
A numerical analysis of the luminescence intensity from the written domains showed that for both studied glasses, an increase in the pulse energy up to 200 nJ leads to the formation of domains with a maximum luminescence intensity. Importantly, the observed luminescence (figure 2(b)) suggests the formation of small CdS nanoparticles and silver nanoclusters in laser-written domains. A further increase in the pulse energy resulted in luminescence quenching, which could be related to the formation of large CdS particles in OS-1CdS glass and the beginning of aggregation of silver nanoclusters into larger agglomerates in OS-0.1Ag glass. It should be noted that the simultaneous formation of both small and large nanoaggregates generally occurs in the laser-written domain due to the Gaussian energy distribution in the laser beam and the corresponding temperature profile.

Figure 3. Dependence of the luminescence intensity of written domains on the number of laser pulses at a pulse energy of 400nJ.

We also performed an analysis of the evolution of the luminescence intensity with a number of writing laser pulses for the domains written with $10^1$ to $10^6$ pulses at a pulse energy of 400 nJ (figure 3). One can see that the larger the number of pulses, the higher the luminescence intensity. The rate of the increase in the luminescence intensity is lower for OS-1CdS glass than for OS-0.1Ag glass when the number of pulses is $10^5$-$10^6$. This phenomenon can also be tentatively explained by the formation of large CdS nanoparticles causing quenching of luminescence from smaller particles.

When comparing the results obtained for OS-0.1Ag and OS-1CdS glasses, it is important to take into account the concentration of the dopant. In this work, the concentration of silver in OS-0.1Ag glass was 10 times lower than the concentration of CdS in OS-1CdS glass, but when comparing the luminescence intensities of the written domains, we obtained relatively similar results. Thus, the determination of the optimal concentration of a particular dopant in glass is required for achieving the maximum luminescence intensity of the written domains. By varying the parameters of DLW (pulse energy and number of pulses), it is possible to record data in the luminescence intensity signal of written domains at several intensity levels, which opens the way for multilevel data recording in the bulk of robust and chemically stable silicate glass.

4. Conclusions
We showed that femtosecond DLW is a useful technique for one-step spatially-selective formation of micron-sized luminescent domains in the bulk of Ag-doped and CdS-doped silicate glasses, using the example of K$_2$O-ZnO-B$_2$O$_3$-SiO$_2$ glass. It is demonstrated for both studied glasses that the precipitation and growth of luminescent Ag nanoclusters and CdS quantum dots occur in the periphery
of laser-written domains under the irradiation conditions of $10^1$-$10^6$ laser pulses at a pulse energy of 100 - 400 nJ. We managed to control the size and optical characteristics of laser-written domains by varying the pulse energy and the number of pulses. An increase in the number of laser pulses from $10^1$ to $10^6$ leads to a tenfold increase in the luminescence intensity of the written domains. The obtained results point to possible applications in multilevel optical data recording.

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References
[1] Ekimov A I and Onushchenko A A 1981 JETP Lett. 34(6) 345
[2] Ricard D, Roussignol P and Flytzanis C 1985 Opt. Lett. 10 511
[3] Belharouak I, Parent C, Tanguy B, Le Flem G and Couzi M 1999 J. Non-Cryst. Solids 244 238
[4] Borrelli N F, Hall D W, Hoiland H J and Smith D W 1987 J. Appl. Phys. 61, 5399
[5] Lipatiev A S, Lipateva T O, Lotarev S V, Okhrimchuk A G, Larkin A S, Presnyakov M Yu and Sigaev V N 2017 Cryst. Growth Des. 17(9) 4670
[6] Lipatiev A S, Lotarev S V, Okhrimchuk A G, Lipateva T O, Fedotov S S and Sigaev V N 2018 Cryst. Eng. Comm. 20(22) 3011
[7] Almeida J M P, de Boni L, Avansi W, Ribeiro C, Longo E, Hernandez A C and Mendonca C R 2012 Opt. Express 20(14) 15106
[8] Tan D., Sharafudeen K N, Yue Y and Qiu J. 2016 Prog. Mater. Sci. 76 154
[9] Shakhgildyan G Yu, Lipatiev A S, Vetchinnikov M P, Popova V V, Lotarev S V, Golubev N V, Ignat’eva E S, Presnyakov M Yu and Sigaev V N 2018 J. Non-Cryst. Solids 481 631
[10] Miyamoto Y, Takei Y, Nanto H, Kurobori T, Konnai A, Yanagida T, Yoshikawa A, Shimotsuma Y, Sakakura M, Miura K, Hirao K, Nagashima Y and Yamamoto T 2011 Radiat. Meas. 46 1480
[11] Dai Y, Hu X, Wang C, Chen D, Jiang X, Zhu C, Yu B and Qiu J 2007 Chem. Phys. Lett. 439 81
[12] Vetchinnikov M P, Lipatiev A S, Shakhgildyan G Yu, Golubev N V, Ignat’eva E S, Fedotov S S, Lipateva T O, Lotarev S V, Vilkovisky G A and Sigaev V N 2018 Opt. Lett. 43 2519
[13] Sigaev V N, Savinkov V I, Lotarev S V, Shakhgildyan G Yu, Lorenzi R and Paleari A 2013 Nanotechnology 24(22) 225302