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Femtosecond laser microengineering of silver-containing microporous quartz glasses

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The features of the formation of point microstructures by femtosecond laser radiation on the surface and in the subsurface layer of nanoporous quartz glasses impregnated with silver precursor molecules under air and water conditions are considered. The role of water in changing the morphology of the resulting microstructures based on silver nanoparticles has been demonstrated. In contrast to crater structures formed in the air, in an aquatic environment, convex conical microstructures up to $2\,\mu$m in height appear in the center of the laser irradiation area. Models are proposed to explain the obtained effects.

Keywords: nanoporous quartz glasses, femtosecond laser radiation, aqueous medium, silver nanoparticles, microstructures.

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The processed material exposed to laser radiation in the course of fabrication of microstructures (microengineering) is often immersed in various media [1–5]. An aqueous medium has several attractive properties, such as high transparency, photoresistance and chemical resistance, and high values of density and thermal conductivity. For example, an aqueous solution of silver salts is often used as a medium in laser-assisted formation of microstructures in transparent dielectrics [3,6,7]. Silver nanoparticles (Ag NPs) form in this case in the irradiated region at the dielectric–water interface, and thermoplasmonic processes and photochemical reactions, which induce modification and destruction of surface layers of the processed material [8], are facilitated.

In the present study, we report the first results of application of an aqueous medium in laser-induced formation of microstructures in quartz nanoporous glasses (NPGs) with organic silver-containing molecules in their pores. The aim of the study is to demonstrate the differences in physical processes and morphology of microstructures produced in air and aqueous media under femtosecond laser irradiation. The mechanisms of formation of microstructures of various morphologies in NPG samples will be discussed in more detail (with account for thermoplasmonic effects developing in an aqueous medium) in a separate paper.

Russian-made RF-RKhTU [9–11] quartz NPGs containing 98% of SiO_2 with diameters of interconnected pores ranging from 4.5 to 10 nm and a porosity of 20–25% and well-known Vycor NPGs produced by Corning (United States) [12,13], which contain 96.3% of SiO_2 with a pore size of ~ 5 nm and a porosity of 28%, were used. Samples in the form of polished plates $5 \times 10 \times 1$ mm in size were impregnated in a medium of pure (99.9999%) supercritical CO_2 with molecules of the Ag(hfac)COD-(1,5-cyclooctadiene) (1,1,1,5,5,5-hexafluoroacetylacetonate) silver(I) organometallic silver compound produced by Aldrich (United States) in powdered form. With this aim in view, they were introduced into a 5 ml reactor together with 6 mg of the silver-containing precursor powder. Impregnation was performed at 50°C and a pressure of 200 bar for 90 min in accordance with the procedure detailed in [9].

A TEMA-100 (Avesta-Project, Russia) femtosecond laser was the radiation source. Second harmonic radiation with $\lambda = 525$ nm (pulse repetition rate $f = 70$ MHz, pulse duration $\tau = 80$ fs, and pulse energy $E = 0.95$ nJ) was introduced into a 20X objective (ZEISS 422050-9903-000, EC EPI PLAN 20x/0.4) with a working distance of 3.2 mm positioned above a three-axis table.

In experiments with an aqueous medium, the sample in a cuvette with distilled water was positioned so that its upper surface was level with the water surface. The time of complete impregnation of NPG samples with water did not exceed 15 min.

A ToupTek XFCAM1080PHB (China) digital camera with a long-focus microlens was used for visual monitoring of the process of microstructure formation. Microstructures were examined with an HRM-300 Series (Huvitz, Korea) 3D microscope with a U3CMOS05100KPA digital camera (ToupTek, Singapore).

Experiments revealed that the characteristics of microstructures formed on the NPG surface depend to a large extent on the medium used. Figure 1 presents photographic

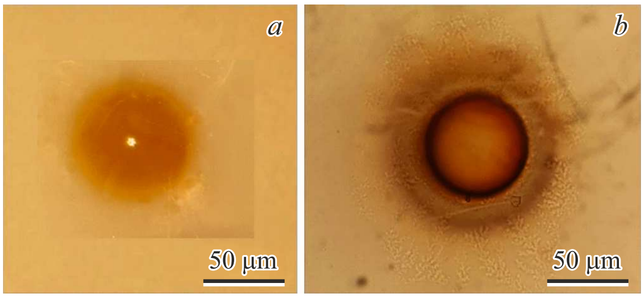

Figure 1. Optical photomicrographs of point-like microstructures on the surface of the RF-RKhTU sample obtained in air (*a*) and in water (*b*). The structures were illuminated from the top. The irradiation parameters were $P = 80$ mW and $t = 0.5$ s; the irradiation dose was ~ 40 mJ.

images of microstructures formed on the surface of the RF-RKhTU NPG sample after irradiation in two media.

A point-like structure in the form of a diffusely colored light-brown spot with an absorption band with a maximum around 410 nm formed on the surface of the plate processed in air (Fig. 1, *a*). This is attributable to the formation of plasmonic Ag NPs similar to those obtained earlier [9]. In the aqueous medium (Fig. 1, *b*), darker ring structures emerged against the background of the diffuse spot. In addition, ill-defined fractal-like structures, which branched radially from the edge of the diffuse spot, were noted in a wider region.

The following qualitative models of the mechanisms of formation of spots with ring, fractal, and volumetric structures (Fig. 1, *b*) on the surface of NPG samples under irradiation in an aqueous medium are proposed at this point. With laser radiation focused inside the sample, plasmonic Ag NPs form due to photodecomposition and thermal decomposition of precursor molecules. The resulting Ag NPs actively absorb laser radiation, which leads to an increase in temperature in the exposed area. Liquid flows emerge due to the presence of water in nanopores and Marangoni convection [14,15] on the surface of the sample (owing to the surface tension gradient). These flows lift the liquid up to the NPG surface in the region of the optical axis and spread it radially sideward. Since the viscosity of water decreases rapidly with temperature, such flows induce the formation of fractal-like structures as a result of hydrodynamic instability with a less mobile liquid displaced by a more mobile one [14]. Note that the mechanism of formation of ring structures (Fig. 1, *b*) is probably the same as the one shaping „Marangoni rings" that are known to emerge when a colloidal droplet dries. Owing to the Marangoni flow, colloidal particles accumulate in the form of rings between the contact line and the droplet center [14,15].

The morphology of the central part of point-like microstructures on the NPG surface changed radically when the air medium was switched to the aqueous one. In air, a depression, which usually forms as a result of laser ablation due to material removal [16], was observed at the center of the structure (Fig. 2, *b*). In contrast, laser irradiation in the aqueous medium led to the emergence of a cone-shaped protrusion with a height of $\sim 1.5\,\mu$m at the center (Fig. 2, *a*). This transformation of morphology in transition from laser irradiation in air to processing in the aqueous medium was observed for both types of NPGs.

The model presented in Fig. 2, *c* provides an explanation for the discovered effects of morphological transformation of structures on the NPG surface. In the air medium, the maximum ($T_{\max}$) of temperature in its vertical profile is reached at the NPG/air interface due to weak outflow of heat into the air. If $T_{\max} > T_{th}$ (the threshold level), ablation

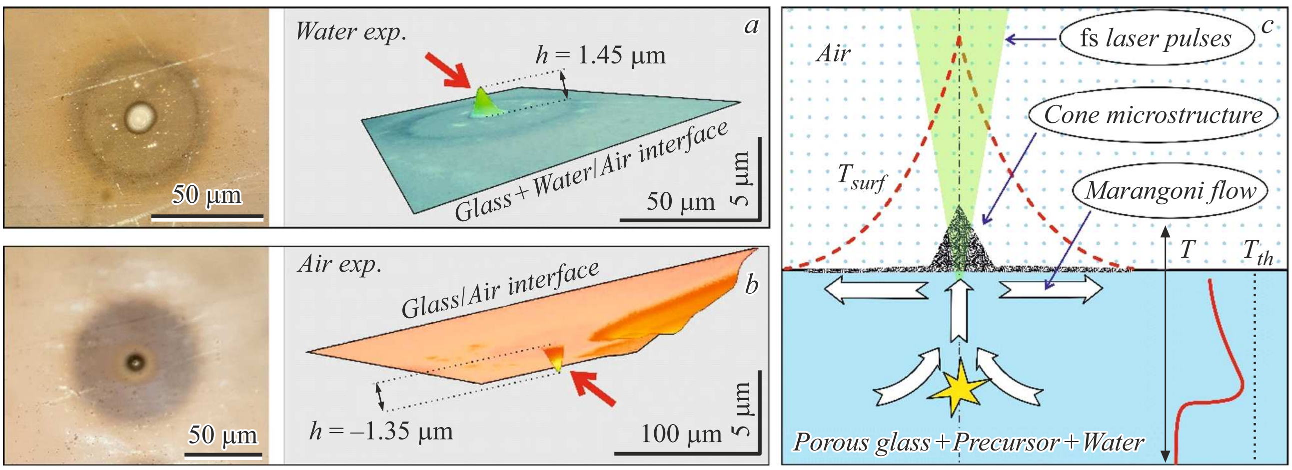

Figure 2. Specific features of morphology of microstructures on the NPG surface under point laser irradiation in water and air media. *a*, *b* — Optical images of microstructures and their three-dimensional topographic images. *c* — Diagram illustrating the processes leading to the formation of a cone-shaped protrusion in the aqueous medium. The air medium is at the top, and porous glass saturated with an aqueous solution of the silver precursor is at the bottom. The T_{surf} surface temperature profile (dashed curve), the temperature profile along the optical axis (solid curve; ablation threshold T_{th} is indicated), and liquid flows in the NPG (light arrows; the region with the maximum temperature is marked with an asterisk) are shown schematically. $P = 80$ mW, $t = 5$ s, and the irradiation dose was 40 mJ.

with the formation of a crater is observed. With a switch to the aqueous medium, the maximum temperature shifts into the bulk of NPG due to greater cooling and significant heat outflow associated with the evaporation of water at the upper boundary of the sample. No ablation is observed at $T_{\max} < T_{th}$. At the same time, the presence of water in the NPG should induce the formation of a colloidal flow (see above) directed upward in the region of the optical axis. This jet lifts Ag NPs and fragments of precursor molecules to the surface of the sample, where they are spread radially by colloidal flows. When a surface is exposed to a laser beam with a Gaussian intensity distribution, the maximum temperature is established at the center of the laser spot. The maximum rate of water evaporation is also observed at this site. Therefore, the concentration of Ag NPs may increase significantly at the center on the surface of the protruding colloidal „fountain" [17], leading to gradual formation of the observed cone-shaped structure (Fig. 2, *a*).

Thus, a new approach to laser formation of microstructures on the NPG surface was presented. It was demonstrated that ring and fractal structures form under femtosecond laser irradiation of such materials impregnated with molecules of organometallic silver compounds in an aqueous medium and that a cone-shaped protrusion possibly containing Ag NPs may form at the center.

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Conflict of interest

The authors declare that they have no conflict of interest.

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