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# On the mechanisms of single-pulse laser-induced backside wet etching

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ABSTRACT

Laser-induced backside wet etching (LIBWE) of a silicate glass surface at interface with a strongly absorbing aqueous dye solution is studied. The process of crater formation and the generated optoacoustic signals under the action of single 5 ns laser pulses at the wavelength of 527 nm are investigated. The single-pulse mode is used to avoid effects of incubation and saturation of the etched depth. Significant differences in the mechanisms of crater formation in the “soft” mode of laser action (at laser fluencies smaller than 150–170 J/cm$^2$) and in the “hard” mode (at higher laser fluencies) are observed. In the “soft” single-pulse mode, LIBWE produces accurate craters with the depth of several hundred nanometers, good shape reproducibility and smooth walls. Estimates of temperature and pressure of the dye solution heated by a single laser pulse indicate that these parameters can significantly exceed the corresponding critical values for water. We consider that chemical etching of glass surface (or molten glass) by supercritical water, produced by laser heating of the aqueous dye solution, is the dominant mechanism responsible for the formation of crater in the “soft” mode. In the “hard” mode, the produced craters have ragged shape and poor pulse-to-pulse reproducibility. Outside the laser exposed area, cracks and splits are formed, which provide evidence for the shock induced glass fracture. By measuring the amplitude and spectrum of the generated optoacoustic signals it is possible to conclude that in the “hard” mode of laser action, intense hydrodynamic processes induced by the formation and cavitation collapse of vapor-gas bubbles at solid–liquid interface are leading to the mechanical fracture of glass. The LIBWE material processing in the “soft” mode, based on chemical etching in supercritical fluids (in particular, supercritical water) is very promising for structuring of optical materials.

## 1. Introduction

Laser radiation has long been used for structuring of various types of materials [1–4]. Different laser-induced physical and chemical processes, based on ablation, modification, or deposition of materials, are applied for producing bulk and surface microstructures at multiple spatial scales [5–7]. More recently, the laser-induced backside wet etching method (LIBWE) has been developed for the formation of microstructures at the surface of optically transparent materials [8–11]. In the LIBWE method, laser pulses are tightly focused on the back surface of an optically transparent sample at the interface with a strongly absorbing liquid. Laser radiation heats liquid at the liquid-material interface, which results in the energy transfer to the sample material and its ablation. This allows forming of various types of microstructures at the surface of transparent samples by imprinting interference patterns [12] or moving laser focus [13].

Laser fluencies required for the effective LIBWE process depend on sample material and applied liquid (for fused silica and nanosecond laser pulses they are in the range of 0.5–10 J/cm$^2$ for multi-pulse irradiation). The fabricated microstructures in optical materials are characterized by low surface roughness (less than 10 nm rms) [14] and high aspect ratio (up to 33) [15,16]. Therefore, LIBWE is promising for the creation of new types of microstructures for microelectronics; fiber-, integrated-, and micro-optics [14,17,18]; microfluidics [19], etc. Particularly promising is the application of LIBWE method in cases when it is difficult to apply standard etching techniques, for example, for manufacturing of channel waveguides in quartz glass activated with rare earth elements. At the same time, the mechanism of material removal and crater formation during the LIBWE process is not clear. The LIBWE models discussed in [10,20,21] are based on experiments with a large number of laser pulses where subsequent laser pulses interact with pulse-to-pulse modified surface structures. Therefore,

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for investigations of the LIBWE process, it is important to conduct single-pulse laser etching experiments to eliminate influence of incubation and saturation effects on the produced structures [22]. This also allows controlling hydrodynamic effects at the sample-liquid interface using optoacoustic techniques [23].

In this paper, experimental investigations of the LIBWE method applied for the formation of craters in silicate glass samples, at the interface with a strongly absorbing aqueous dye solution, are performed. Conclusions about LIBWE mechanisms are made on the basis of crater formation experiments under the action of single laser pulses in a wide range of laser fluencies. Simultaneously, hydrodynamic effects at the glass-liquid interface are analyzed using optoacoustic methods.

## 2. Experimental

Fig. 1 shows a block diagram of the experimental setup used for studies of the LIBWE process. Laser pulses are focused on the backside surface of an optically transparent sample (7a) at the interface with a strongly absorbing liquid (7b). Experiments are conducted in a single-pulse mode with the second harmonic of the diode-pumped solid-state laser (TECH-527 Basic, Laser-compact, Russia) at the wavelength of 527 nm, pulse duration of ~5 ns, maximum pulse energy of 250 μJ, and beam divergence of $<3$ mrad. Laser beam with a near Gaussian profile passes through the beam expander (1) and diaphragm (2). By changing the beam diameter, focus parameters can be varied (see below). By the plane-parallel beam splitter (3), a part of the beam is directed to the energy meter QE8SP-B-MT-INT (Gentec) (4). The transmitted radiation, after a spectrally selective (dichroic) mirror (5) and 10 × lens (6) with NA=0.25, is focused at the glass-liquid interface. The selective mirror (5) allows imaging of the irradiated surface area with the USB 2.0 camera EXCCD (ToupTek) (10), using white light illumination (11), for on-line observation of the etching process. After each laser pulse, the focus position on the glass plate was changed using the computer-controlled translation stage (8).

For investigations of the LIBWE process, microscope slides made of silicate glass were used as samples (7a) placed at the front of the demountable cell (7) filled with the strongly absorbing liquid (7b). The cell (7) was placed on the three-axis translation stage (8), 8MT167-100 (Standa), with the positioning accuracy better than 0.5 μm. As a strongly absorbing aqueous solution, the food dye Amaranth (Sigma-Aldrich) was applied [24]. The absorption spectra of the dye solutions were measured using UV-3600 (Shimadzu) spectrophotometer. The absorption coefficient of the saturated dye solution (100 mM) at the 527 nm wavelength is $2\cdot10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$. This ensured absorption of about 90% of laser radiation in a liquid layer with the thickness of about 10 μm.

The diagnostics of the LIBWE process *in situ* was carried out using optoacoustics methods. Acoustic signals were recorded using a 1 mm needle PVdF (polyvinylidene fluoride) hydrophone (Precision Acoustics) (12) with 100 MHz broad-band preamplifier (13). The hydrophone has a flat ±4 dB spectral response in the range of 200 kHz to 15 MHz and sensitivity of 850 nV/Pa. The sensitive end of the needle hydrophone was placed in liquid at a distance of 7 mm from the optical axis. The hydrophone signals were recorded with the 300 MHz bandwidth oscilloscope (14), GDS 72304 (GW Instek). The pressure value was recalculated to a distance of 10 μm assuming spherical wave propagation.

The geometry, shape, and surface characteristics of the LIBWE generated craters were studied using optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Fig. 2 shows an optical image of the generated craters at different laser fluencies. The SEM crater images shown in Fig. 3 were obtained with the scanning electron microscope Phenom ProX at an accelerating voltage of 10 kV. The AFM images shown in Fig. 4 were produced using the scanning probe nano-lab "INTEGRA-Terma" (NT-MDT, Russia) equipped with silicon cantilevers (Veeco RTESP), with the resonant frequency of 300÷360 kHz, and the

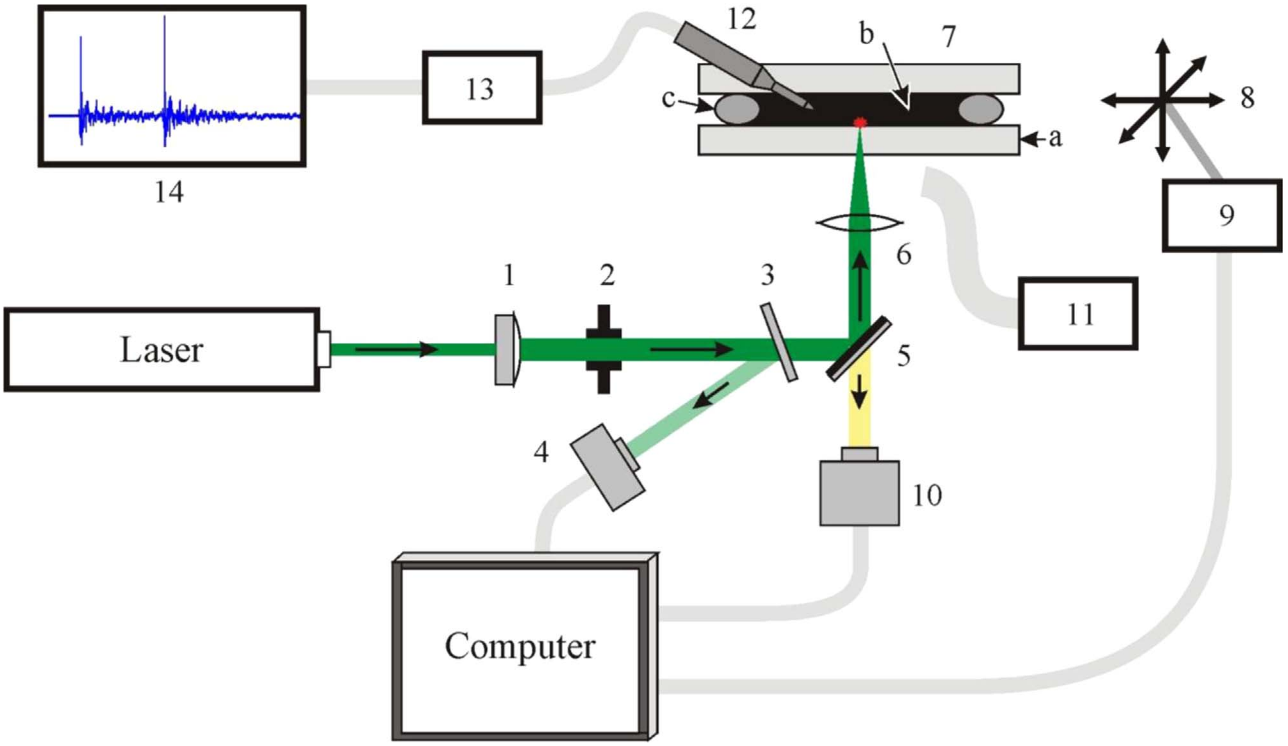

**Fig. 1.** Block diagram of the experimental setup consisting of: beam expander (1), iris diaphragm (2), beam splitter (3), energy meter (4), dichroic mirror (5), focusing lens (6), cell filled with strongly absorbing liquid (7) (a - silicate glass plate, b - absorbing liquid, c - gaskets), three-axis motorized translation stage (8), translation stage control unit (9), USB camera (10), optical lighter with a fiber bundle (11), needle hydrophone (12), preamplifier (13), oscilloscope (14).