Micro-Raman spectroscopy of single-shot pulse silicon craters produced by femto-picosecond laser in air and liquid

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Abstract. Ultra-short pulses are increasingly being used for surface treatment of materials. At the same time, it is not completely clear how a change in the duration and the medium in which ablation occurs affects the morphology of craters and the change in the phase composition of the irradiated surface. A detailed comparison of single shot pulse silicon ablation by laser pulses (pico (10 ps) and subpicosecond (0.3 ps) duration) with a wavelength of 1030 nm in air and water, focused by a lens with a numerical aperture $NA = 0.25$, was demonstrated in this work. The morphology and topography of the formed craters were studied using scanning electronic microscopy. The values of the ablation thresholds were obtained. Addition, two-dimensional Raman maps were obtained and it was shown that the rim of the craters consists of nanocrystallites.

1. Introduction

Ultrashort laser pulses are widely used for surface treatment of materials [1-3]. Typically they are used for precision surface treatment of various kinds of materials. The advantages of surface modification by ultrashort pulses include less thermal damage of the material, improved quality of surface treatment, and less contamination of the target surface by ablation products [4-6]. These advantages running out from the extremely high intensity of ultrashort pulses, and also due to the fact that the duration of ultrashort pulses can be compared with the electron-phonon relaxation time in the material, which is $0.1-10$ ps [2]. A change in the duration of laser radiation in the pico-subpicosecond range significantly affects the ablation process. For example, in [7-9], a significant change in the ablation efficiency was shown when the duration was changed from $0.3$ to $\approx 10$ ps. One of the possible reasons is the change in the ablation mechanism [7, 8]. Changes in the ablation mechanism can also affect structural changes in the irradiated material. For many applications, not only the shape of the structures is important, but also the phase composition [10]. Also, during laser irradiation, mechanical stresses, both tensile and compressive, can occur. As is known, not only the parameters of laser radiation, but also the medium in which the ablation is performed, affect those obtained under laser exposure, which also requires study [10].

Silicon was chosen as a target because due to its unique properties is widely used in micro-optoelectronics, electronics, solar energy [11]. Besides silicon nanoparticles are used in theranostics [12] and in microbiology due to their antibacterial properties [13]. In this work, we analyzed single-shot pulse craters using micro-Raman spectroscopy and scanning electron microscopy. Craters were obtained using femto (0.3 ps) and picosecond (10 ps) single-shot pulse ablation through an objective with a numerical aperture $NA 0.25$. Ablation was carried out both in air and under a layer of distilled water.
2. Experiment
In this experiment, single-shot pulse ablation of fresh sections of a polished wafer of single-crystal unalloyed silicon (orientation [110]) with a thickness of 380 μm with a natural oxide layer of 2-3 nm was performed. The experiments were carried out both in air and in distilled water, where the liquid layer above the sample surface was ≈1-2 mm. In our work, we used a fiber laser Satsuma (Amplitude Systemes) with an active medium based on Yb$^{3+}$ ions (the main wavelength: 1030 nm. The duration of ultrashort laser pulses was varied by an output compression in the interval of 0.3–10 ps [7]. The energy of ultrashort laser pulses in the TEM00 mode was smoothly varied by means of a thin-film reflection attenuator. Laser radiation was focused on the sample surface through an NA = 0.25 objective with focal length 7.50 mm into a spot with a 1/e radius of about 3.2 μm. The topology of the surface was visualized by a scanning electron microscope (JEOL 7001F).

3. Results and discussion
Single-shot pulse craters obtained in air and in water (Fig. 1) have a round shape. At ablation in air at high energies in a pulse range of 9.9 J/cm$^2$, they form a slightly uneven rim. As the energy decreases, the rim becomes smoother, this applies both at ablation at 0.3 ps and at 10 ps. Moreover, for 10 ps, the crown is more manifested, which occurs on the rim of the crater at high energies.

![Fig. 1. SEM visualization of craters obtained at ablation in air and water: Left: for a duration of 0.3 ps; Right: 10ps. White mark: 1µm](image-url)
means the presence of crystallites [14-15]. The largest changes in the spectrum occur on the rim of the crater obtained at 0.3 ps (FWHM ≈16.8 cm⁻¹). This peak was approximated by two Lorentzian functions (520.3 and 512 cm⁻¹ with FWHM 6.7 and 15.7 cm⁻¹ respectively).

Fig. 2. Raman spectra a) ablation in air \(\tau_{\text{las}} = 0.3\) ps b) ablation in water \(\tau_{\text{las}} = 0.3\) ps c) ablation in air \(\tau_{\text{las}} = 10\) ps d) ablation in water \(\tau_{\text{las}} = 10\) ps (white marks: 5 microns)

Ablation thresholds were calculated from dependencies of \(R^2\) on the natural logarithm of the energy \(\ln E\).

Fig. 3. The dependence of the square of the crater radius on the logarithm of energy during ablation in air and in water for a duration of 0.3 ps and 10 ps.
For a duration of 0.3 ps, we observe two curves for the dependences $R^2 - \ln E$ for both ablation in air and ablation in a liquid fig.3. The appearance of two regions means the implementation of two different mechanisms of energy absorption (two-photon absorption) or deformation of the laser beam in the presence of nonlinear effects in the medium (appearance of plasma on the surface, ionization of the medium, etc.).

The obtained values of $F_{th1}$ during ablation in water for a pulse duration of 0.3 ps are significantly higher than during ablation in air (Air $0.15 \pm 0.1$ J / cm$^2$ and water $0.8 \pm 0.1$ J / cm$^2$), which is associated with the appearance of filamentation, which interferes with the ablation process, deforming the laser beam. For picosecond pulses, the ablation threshold in water is slightly lower than during ablation in air ($1 \pm 0.2$ J / cm$^2$ versus $1.2 \pm 0.1$ J / cm$^2$), which compares well with the results of other authors. It is also worth noting that for ablation in water, the focusing spot size parameter $w_{th}$ is larger than in air due to a decrease in the effective $NA$ in the liquid [7].

4. Conclusion

In this work, the silicon surface was treated with ultrashort pulses (0.3, 10 ps) at a laser wavelength of 1030 nm in the single-shot pulse mode. The radiation was focused through a lens with a numerical aperture $NA = 0.25$. Ablation was carried out in air and water. A detailed comparison of the resulting craters was made. The values of the silicon ablation thresholds for femto- and picoseconds for air and water are obtained. Cross-crystallized silicon was found at the edges of the crater.

Acknowledgements

This work was financially supported by the grants of the Russian Foundation for Basic Research (№18-29-20022). The presentation and publication of these results was supported by the conference RFBR grant № 20-02-22038.

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