

# The features of nanoclusters and periodic structures formed at the surface of the crystal and amorphous silica by resonant CO<sub>2</sub> laser irradiation

A.F.Mukhamedgalieva<sup>1</sup>, A.M.Bondar<sup>1</sup>, M.A.Kononov<sup>2</sup>, V.B.Laptev<sup>3</sup>, N.N.Novikova<sup>3</sup>,  
I.M.Shvedov<sup>1</sup>

<sup>1</sup>Moscow State Mining University, Leninsky prospect 6,

P.O. 119991, Moscow, Russia, email: [anel-mggu@mail.ru](mailto:anel-mggu@mail.ru),

<sup>2</sup>Institute of General Physics of Russian Academy of Sciences

P.O. 119991, Vavilov Street 38, email: [mikl@capella.gpi.ru](mailto:mikl@capella.gpi.ru),

<sup>3</sup>Institute of Spectroscopy of Russian Academy of Sciences

P.O. 142190, Moscow region, Troitsk city, Russia, email : [laptev@isan.troitsk.ru](mailto:laptev@isan.troitsk.ru)

## Abstract

The pulsed CO<sub>2</sub> laser irradiation (1 J, 70 ns, laser spot of 1.4 mm) of crystal and amorphous silica lead to creation both of the periodic microstructures and the nanoclusters at the irradiated surface.

## 1. Introduction

The photochemical transformations caused by continuous CO<sub>2</sub> laser radiation ( $10^5$ - $10^6$  W/cm<sup>2</sup>) and pulsed CO<sub>2</sub> laser radiation ( $10^7$  W/cm<sup>2</sup>, 200 ns,) at the surface of the natural silicates (nepheline - Na[AlSiO<sub>4</sub>], rodonite - CaMn<sub>4</sub>[Si<sub>5</sub>O<sub>15</sub>], zircon - ZrSiO<sub>4</sub> etc.) earlier have been investigated. The laser radiation falls on the low frequency side of inhomogeneous broadened infrared absorption line of valent Si-O-Si vibrations in these materials providing effective absorption of laser radiation. The action of laser radiation on these silicates results in the selective sublimation of silicon oxides and the enrichment of surface by the rest elements [1, 2].

In this work the features of nanoclusters and micrometer sized periodical structures formed at the surface of silica (crystal quartz and fused quartz ) by action of pulsed CO<sub>2</sub> laser radiation (pulse energy of 1 J, pulse time of 70 ns) have been investigated. For these aims the high resolution optical microscopic and atomic force microscopic investigations of laser spot and also the investigations of infrared (IR) reflection spectra of surface before and after CO<sub>2</sub> laser irradiation have been made.

## 2. Experimental results

The crystal and amorphous silica have been used as a object of the investigation. The samples mentioned above were irradiated by pulsed CO<sub>2</sub> laser with the pulse duration of 70 ns and pulse energy of 1 J. Effective laser spot diameter was approximately of 1,4 mm. The action of focused laser radiation on the samples lead to rise of the erosion plume at irradiated surfaces providing the photo-induced modification of surface. The samples have been irradiated by CO<sub>2</sub> laser in two regimes – single-mode with fluency of 5,2 J/cm<sup>2</sup> and multi-mode with fluency of 48 J/cm<sup>2</sup> and with two laser frequency - 975 and 1076 cm<sup>-1</sup>.

The features of photochemical transformations induced by pulsed infrared laser radiation at the surface of silica have been investigated by means of the several optical and spectral methods. The image of

laser spot at the irradiated surface by means of as high resolution optical microscope as atomic force microscope has been received. Laser induced structural transformation in silica have been investigated by means of infrared (IR) spectroscopic methods of observation of irradiated surface.

It has been observed that by laser action on the surface of crystal and amorphous silica two kind of periodical structures have appeared – periodical structures with the period length close to wave length of laser irradiation and quasi-periodical nanostructures with the period length close to 100 nanometers. Micron structures have appeared by laser action with more low fluency -  $5,2 \text{ J/cm}^2$  and single-mode laser action, whereas nanostructures have appeared by laser action with more high fluency -  $48 \text{ J/cm}^2$ . The image of laser spot at the surface made by means of high resolution optical microscope revealed the appearance of periodic structure at the irradiated surface with the period length less than wave length of laser irradiation. Two kind of structures are appeared – concentric rings and linear bands. That may be seen at Fig. 1, where the image of several laser spots at the surface are presented and at Fig. 2, where the region of laser spots overlapping are presented. The period length of the received linear bands structures is approximately 7.3 micron for crystal quartz and approximately 8 micron for fused silica irradiated at laser frequency of  $975 \text{ cm}^{-1}$ . The period length of linear structures is approximately 7.1 micron for crystal quartz irradiated at laser frequency of  $1076 \text{ cm}^{-1}$ .

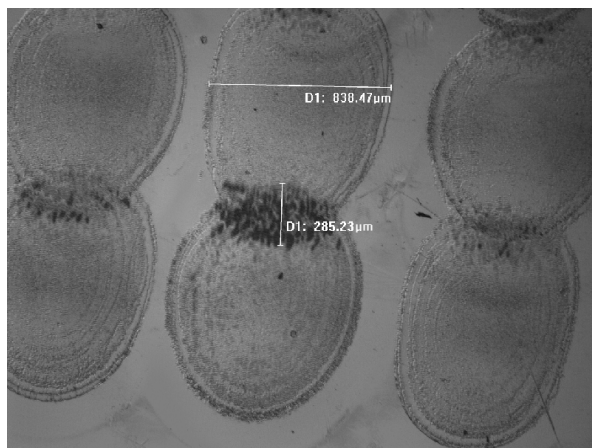


Fig. 1. Microscopical image of 6 laser spot created at the surface of amorphous silica by action of 3 pulses of single-mode  $\text{CO}_2$  laser, fluency  $5,2 \text{ J/cm}^2$ , frequency  $975 \text{ cm}^{-1}$ .

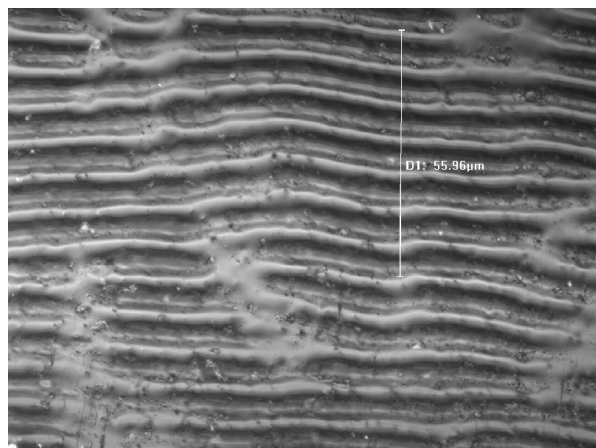


Fig.2. Microscopical image of region of laser spot overlapping after action of 3 pulses of single-mode  $\text{CO}_2$  laser, fluency  $5,2 \text{ J/cm}^2$ , frequency  $975 \text{ cm}^{-1}$ .

The atomic force microscopic (AFM) images of irradiated surface of silicates show the appearance of nanoclusters with size approximately of 50 - 100 nanometers in dependence of type of silicate. The threshold of laser fluency for such nanoclusters formation has value close to  $7-10 \text{ J/cm}^2$ . The maximal highness of nanoclusters at the resonant frequency of laser ( $1076 \text{ cm}^{-1}$ ) has been observed. That it can be seen at Fig. 3 where the image of laser spots at the surface made by means of AFM microscope for laser frequency of  $1076 \text{ cm}^{-1}$  is presented.

For understanding the difference in nanostructures creation at two different frequencies the IR reflection spectra of surface before and after  $\text{CO}_2$  laser irradiation were recorded. The comparison of the IR reflection spectra for irradiated and non-irradiated samples shows the enhancement of reflectance in the region of laser frequency. More high difference have been found at the frequency of  $1076 \text{ cm}^{-1}$ . That can be seen at Fig. 4 which exhibits the fragment of the IR reflection spectra for specimen of quartz irradiated at the frequency of  $1076 \text{ cm}^{-1}$  and non-irradiated that one. At the spectra of quartz irradiated by 3 laser pulse at the frequency of  $1076 \text{ cm}^{-1}$  with the fluency of  $48 \text{ J/cm}^2$  the narrow line with line width of  $20 \text{ cm}^{-1}$  at the frequency of laser has appeared.

The enhancement of reflectance in the region of laser frequency has been named as a stable «line burning» in the IR reflection spectra of samples. The width of burning line is approximately  $20 \text{ cm}^{-1}$ . This «line burning» is revealed in absorption spectra of samples as a decrease of absorption («hole burning») at an incident laser frequency. The most important characteristic features of this hole burning is that the line burning has an accumulating character, namely, the burning intensity depends on

the number of laser pulses incident upon the samples. Note, that the hole burning at an incident laser frequency with many more weakly effect was earlier observed in the absorption spectra of nepheline thin surface layer after its irradiation with a continuous CO<sub>2</sub> laser at an energy fluency rate of 10<sup>5</sup> W/cm<sup>2</sup> [1].

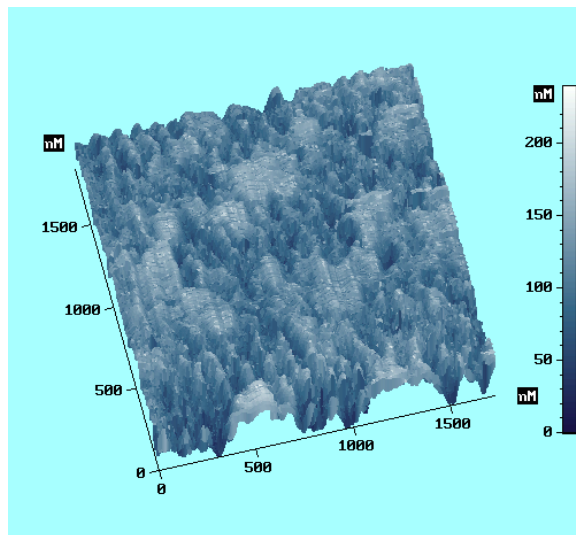


Fig. 3. AFM image of laser spot created at the surface of fused quartz by the action of pulsed CO<sub>2</sub> laser radiation at the frequency of 1076 cm<sup>-1</sup>, fluency of 48 J/cm<sup>2</sup>.

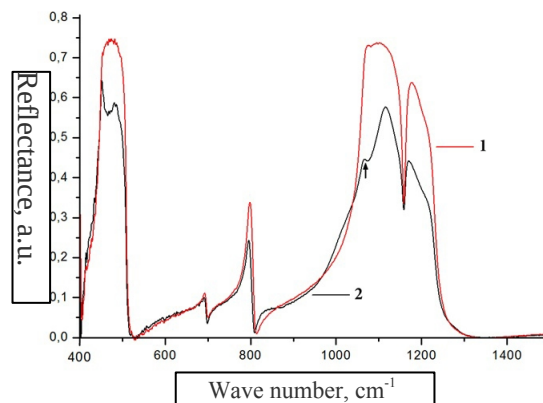


Fig. 4. IR reflection spectra of crystal quartz before and after irradiation by pulsed CO<sub>2</sub> laser at the frequency of 1076 cm<sup>-1</sup>, fluency of 48 J/cm<sup>2</sup>. 1-initial sample, 2-irradiated sample.

### 3. Conclusion

The appearance of periodical structures at the surface of silica by the action of pulsed CO<sub>2</sub> laser allow us to made some conclusion.

1. By laser action on the surface of crystal and amorphous silica two kind of periodical structures are appeared – periodical structures with the period length close to wave length of laser irradiation and quasi-periodical nanostructures with the period length close to 100 nanometers. Micron structures have appeared by laser action with more low fluency - 5,2 J/cm<sup>2</sup> and single-mode laser action, whereas nanostructures have appeared by laser action with more high fluency - 48 J/cm<sup>2</sup>.

2. Periodical microstructures in a crystal and amorphous silica have appeared because of interference of incident waves and surface waves induced by incident waves in resonant absorption media. The increase of ablation velocity at the maxims of standing waves take place.

3. Cumulative properties of periodical structures formation (dependence of relief depth from laser pulses number) allow us to conclude that the mainly ablation take place by laser action on silicates.

4. Dependence of relief depth from frequency of laser action shows that microstructure formation connects with the resonant interaction of CO<sub>2</sub> laser radiation with silicates. Intensive ablation in maxims of standing waves connects with the breaking of covalent oxygen – silicon bonds in region of laser action frequency what can be proved by IR spectra of irradiated samples.

Received structures give the possibility to make the materials with novel properties applicable in integral optics, photonics, and other fields.

### References

- [1] A.F. Mukhamedgalieva and A.M. Bondar', Laser-stimulated reaction on the surface of quartz and some minerals, *Surface (Russian physics), Physics, Chemistry, Mechanics*, no. 5, pp. 125-129, 1983.
- [2] A.F. Mukhamedgalieva and A.M. Bondar', Laser-induced selective sublimation from silicates, *Proceedings of SPIE*, vol. 2118-33, pp. 224-226, 1994.