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# Laser ablation studies of nanocomposites

Oleg V. Mkrtychev [a], Vadim E. Privalov [b,*], Alexander E. Fotiadi [b], Valery G. Shemanin [a]

[a] *Novorossiysk Polytechnic Institute, 20 Carl Marx St., Novorossiysk 353900, Russian Federation*
[b] *St. Petersburg Polytechnic University, 29 Politekhnicheskaya St., St. Petersburg 195251, Russian Federation*

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## Abstract

The first experimental measurements of the threshold energy density values for the laser ablation of glass nanocomposites with nanodimensional coatings have been carried out under the action of the YAG–Nd laser power pulse radiation. The coatings in question were of different compositions and had been created by the sol–gel technology. The procedure for determining the laser ablation threshold energy density values was worked out on the base of the breakdown probability level of 0.5. The statistical processing of the measurement data over all the samples allowed obtaining the dependence of the ablation destruction threshold energy parameters on the coating physical and chemical properties such as the sample transmission in the visible region of the spectrum, coating thickness, the chemical composition of the film-forming solution, and on the pulse duration of laser radiation.

*Keywords:* Laser ablation; Glass nanocomposite; Nanodimensional coating; Threshold energy density; Breakdown probability; Transmission; Film-forming solution; Chemical composition.

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## 1. Introduction

The materials laser processing technologies based on the laser ablation are widely used in high-tech industry operations such as microprocessing and modification of parts and their surfaces, thin-film coatings [1,2]. As it was noted by the authors [1,2], an important aspect of the problems associated with laser ablation is the probabilistic nature of destruction processes. There are several reasons for this: random spatial distribution of absorbing defects, different characteristics of these defects leading to different threshold laser breakdown values, probabilistic nature of the birth of seed electrons which initiate the development of plasma avalanche ionization, and the close relationship between the breakdown threshold and laser interaction area size (size effect).

Earlier works [3–6] were performed to study polymeric materials laser ablation under the action of high-energy pulsed laser radiation and to develop probabilistic methods for predicting the optical strength of such samples. This required a detailed study of the dynamics and mechanism of plasma generation during polymer laser ablative destruction in the range of laser pulse energy density up to 100 J/cm$^2$.

The aim of the present work is to study experimentally laser ablation threshold characteristics of some glass nanocomposites of different compositions, made by sol–gel technology [7], under the action of YAG–Nd laser pulsed radiation, and to study the dependence of

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[*] Corresponding author.

*E-mail addresses:* oleg214@ya.ru (O.V. Mkrtychev), vaevpriv@yandex.ru (V.E. Privalov), fotiadi@rphf.spbstu.ru (A.E. Fotiadi), vshemanin@nbkstu.org.ru (V.G. Shemanin).

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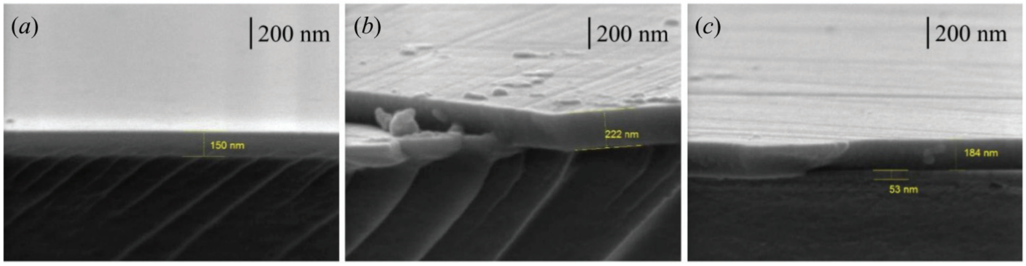

Fig. 1. Sectional microphotographs, obtained from X-ray phase analysis, of some oxides deposited on glass substrates: a thin film of $SiO_2$ (*a*), the same of $TiO_2$ (*b*), a layer of $TiO_2$ on the one of $SiO_2$ (*c*). The layer thicknesses are as follows: 150 nm (*a*), 222 nm (*b*), 184 nm and 53 nm (*c*).

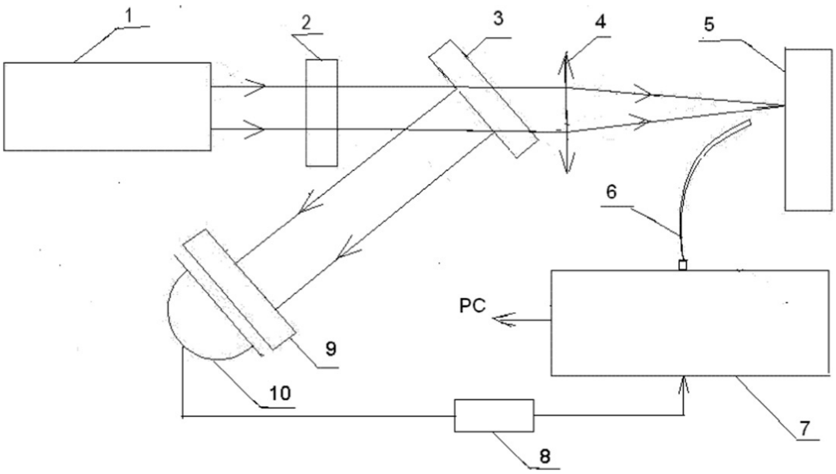

Fig. 2. Laboratory laser-ablation equipment: laser (*1*), neutral filter to change the energy of the radiation (*2*), glass plate (*3*), focusing lens (*4*), sample (*5*), optofiber (*6*), microspectrometer FSD-8 (*7*), delay line controlled by a PC (*8*), filter IRF-1 (*9*), photodiode (*10*).

these characteristics on the optical and physical properties of nanocomposites.

## 2. Experimental

All the measurements were carried out on nanocomposite samples which were rectangular plates sized from 4 to 7 cm and produced of clear float glass coated with different oxides: a single layer of $SiO_2$ or $TiO_2$, two or three layers of $SiO_2$, a double layer of $SiO_2 + TiO_2$. X-ray microphotographs of the first two and the last samples are shown in Fig. 1 as an example.

Since the coating produced from colloidal solution was deposited on cold glass, after coating the samples were kept in air and then fired in a laboratory furnace at the temperatures of 450–600 °C within 30 min.

For the experimental investigation of nanocomposite laser ablation, measuring the laser radiation threshold energy density was performed at which the breakdown of the sample surface started. Laboratory laser ablation apparatus was assembled on the basis of [3,5,6] experimental set-up and its structural scheme is shown in Fig. 2.

The radiation source was a laser (*1*). YAG–Nd laser generated pulses with the wavelength of 1064 nm of two types:

(a) the pulse duration was 20 ns, the pulse energy was up to 0.15 J;
(b) the corresponding values were 300 μs and 1.2 J.

Generation was produced in two modes of *Q*-switching and with different passive valves. The laser radiation was focused onto the nanocomposite surface by a special lens (*4*). The change in the laser pulse energy density in the range from 0.1 to 100 J/cm$^2$ was achieved by selecting the focal length of the lens (*4*) and by weakening the radiation by calibrated neutral filters (*2*). The presence of the breakdown was recorded via the appearance the laser plasma glow which was recorded by the microspectrometer (*7*) (type FSD-8, production of GPI RAS) with the fiber input (*6*). To control the laser pulse energy and to sync all the laboratory set-up, the photodiode (*10*) with the optical filter (*9*) (type IRF-1) were used. The delay line (*8*) controlled by the computer was required to start the work of the spectrometer (*7*) relative to the laser pulse leading edge. The spectrometer (*7*) operation modes and the measurement results processing were also carried out by the computer.

The nanofilm refractive index $n$ and the thickness $d$ (in nm) were measured with the use of a spectral ellipsometer HORIBA Jobin Yvon. Integral light transmission $T$ (in %) of nanocomposite samples in the visible spectral range of 400–800 nm was recorded with a microspectrometer FSD-8 and processed with a computer.

## 3. The experimental results

In the first phase, calibration experiments were performed on targets made of Teflon AF-4 [5,6] and the threshold energy density $F_b$ of the breakdown was equal to 25 J/cm$^2$ on 0.5 probability in accordance with the Ref. [6]. To generate a breakdown probability curve, one should make at least 20 measurements at a given laser radiation pulse energy and to measure the number of breakdown events on the target surface in relation to the total number of measurements. Setting a new, lower value of energy density and repeating this measurement process, one can sequentially pass the entire range of the breakdown probability values from 1 to 0. If the dependence of the laser breakdown probability on the energy density is not smooth, it means that the measurement error is insufficient, and this in turn means that an increased number of measurements is required. The correct interpretation of this dependence is important for the exact determination of nanocomposites laser ablation threshold energy density values with the probability of 0.5 [6]. Such calibration experiments allowed us to obtain the optimal geometry of the irradiation of the sample that was used in all further experiments.

In the second phase, the breakdown probability dependencies (or curves) described above were obtained for all the samples. One of the curves is shown in Fig. 3 as an example. The dependencies can be interpolated by polynomials. On the graph of Fig. 3, each ordinate is defined as the ratio of the number of those pulses which caused a breakdown and plasma glow to the total number of the pulses for a given sample. As the threshold energy density $F_b$, the intensity was chosen at which the ordinate $P$ was equal to 0.5 [6]. In case of the sample of Fig. 3, two threshold energy densities were found: $F_{b1} = 61.2$ J/cm$^2$ for 300 μs pulses and $F_{b2} = 32.8$ J/cm$^2$ for 20 ns. The relative measurement error was about 12%. So, the conclusion made in Ref. [4] about the decrease of laser ablation threshold energy density with the reduction of the laser pulse duration is confirmed by the curves in Fig. 3.

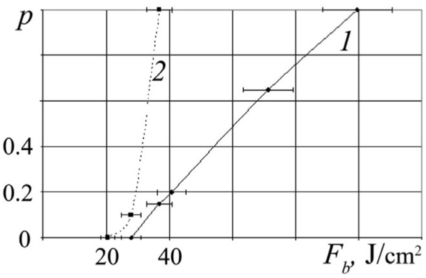

Fig. 3. Plots of breakdown probability (one of the one-layer SiO$_2$ samples) vs. radiation energy density $F_b$ for microsecond (*1*) and nanosecond (*2*) pulses.

Table 1
The average parameter values obtained for the samples of different chemical composition and modes of laser operation.

| Sample | Refractive index $n$ | $F_b$ (J/cm$^2$) | |
|---|---|---|---|
| | | $\tau = 300$ μs | $\tau = 20$ ns |
| SiO$_2$ | 1.46 | 69.0 | 27.4 |
| SiO$_2$ (2) | | 78.4 | 28.5 |
| SiO$_2$ (3) | | 57.1 | 25.3 |
| TiO$_2$ | 1.97 | 85.9 | 31.7 |
| SiO$_2$ + TiO$_2$ | | 85.4 | 24.9 |

Notations: $F_b$ is the threshold energy density for laser ablation, $\tau$ is a pulse duration; parentheses contain numbers of coatings.

Measurements were made with each sample from 20 to 100 times at a given energy value, and after this the radiation focus was transferred onto a new sample point. For each sample, the dependence between breakdown probability and energy density was examined and the same graph as that given in Fig. 3 was built.

Basing on obtained dependence on the level with the probability $P = 0.5$, we had the value of the threshold energy density $F_b$. Table 1 shows the results of processing the measured values for some samples. A comparison of all these data given in Table 1 shows that the average values of the threshold energy density have a maximum for the films of titanium dioxide in case of both pulse durations and for the coating of two layers of silicon dioxide and titanium dioxide.

Maximum growth of $F_b$ is achieved from TiO$_2$ over SiO$_2$ layers in both the microsecond and nanosecond ranges. The obvious link exists between the number of layers of silicon dioxide and the threshold density of the laser radiation. The dependence of the threshold energy densities of laser ablation on the number of silicon dioxide layers has a maximum for two layers, and this can be explained by the approximation of the relationship of the length of the laser pulse to the thickness of all the

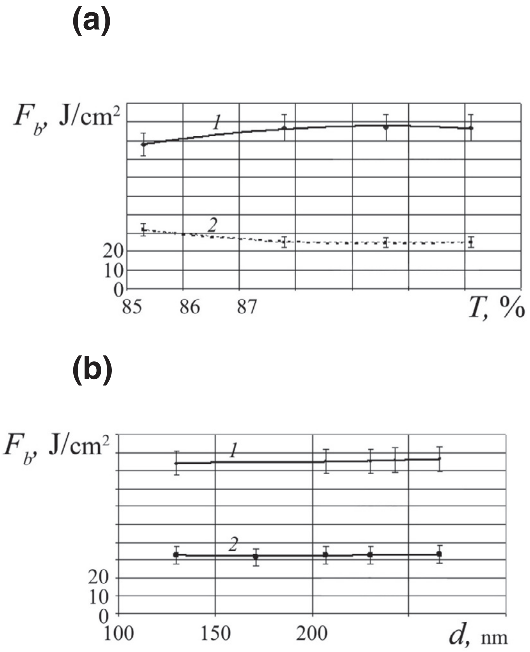

Fig. 4. Plots of the threshold energy density for laser ablation vs. transmission $T$ (*a*) and film thickness $d$ (*b*) of $SiO_2$ films; the data were obtained for five coatings subjected to laser radiation with the pulse durations of 300 µs (curve *1*) and 20 ns (*2*). The equations of the polynomial approximation are presented in Table 2.

layers to 1 when focused laser radiation reaches the surface of the glass. Indeed, the refractive index of silicon dioxide is equal to 1.46 compared to the glass refractive index of 1.55 V. The value of the threshold energy density for laser ablation reduces (in case of three layers of silicon dioxide) due to the fact that a focused laser beam is distributed only in the coating and does not reach the surface of the glass. For microsecond pulses this effect is bigger in comparison with the pulses of nanosecond range.

Let us consider in detail the main results of the measurements. The laser ablation threshold density $F_b$ in the microsecond and nanosecond ranges depending on the sample light transmittance of nanocomposites for five samples of $SiO_2$ coatings is shown in the graphs of Fig. 4*a*.

These dependencies were fitted by a polynomial of the second degree and are presented in Fig. 4*a* by lines. The equations obtained are given in Table 2. From these data, one can see that the threshold density of laser destruction $F_{b1}$ increases with light transmission of the sample for the films of $SiO_2$ when exposed to pulses with the duration of 300 µs, but for the duration of the laser pulse of 30 ns, similar values $F_{b2}$ decrease with transmission.

Table 2
The approximation results for $F_b$ ($T$) and $F_b$ ($d$) in Fig. 4.

| Fig. 4 | | τ | $F_b$ (J/cm$^2$) | $R^2$ |
|---|---|---|---|---|
| (*a*) | *1* | 300 µs | $-0.5574\,T^2 + 99.818\,T - 4381.1$ | 0.9775 |
| | *2* | 20 ns | $0.4012\,T^2 - 71.849\,T + 3240.9$ | 0.9787 |
| (*b*) | *1* | 300 µs | $(6 \times 10^{-5})\,d^2 - 0.008d + 84.070$ | 0.9643 |
| | *2* | 20 ns | $(1 \times 10^{-4})\,d^2 - 0.044d + 36.217$ | 0.4687 |

Notation: $F_b$ is an average value of the threshold energy density for the laser ablation, $\tau$ is the pulse duration; $T$ (%) is the film transmission, $d$ (nm) is the film thickness, $R^2$ is the approximation accuracy.

The same dependences of the threshold density of laser destruction $F_b$ at both pulse durations were obtained for nine samples with the coatings of titanium oxide. In comparison with the previous case, the threshold density of laser destruction $F_b$ is almost constant with the increase of the transmission $T$ of the samples with the accuracy of our measurements of 12% for titanium dioxide and pulse durations of 300 µs and 20 ns. This result may be explained by the fact that the refractive index of all these samples is great and is about 1.97 which is caused by its chemical composition, and so the laser radiation loss will be determined by the reflection from the surface of the coating. According to laser destruction threshold density $F_b$ dependence on the thickness of the silicon dioxide $d$ (in nm) for the duration of the laser pulses of 300 µs and 20 ns (Fig. 4*b*), these dependences are quite gentle, growing slowly with the thickness within the accuracy of our measurements.

This means that the nanocoating thickness has little influence on the laser ablation destruction, which is primarily determined by the sample surface properties. The results given here confirm qualitatively and quantitatively the findings of Ref. [8,9] about the reduction of the threshold energy density leading to laser ablation, with the decrease of the pulse duration.

## 4. Conclusion

Thus, in the present work, the experimental measurements of the threshold energy density of laser ablation of glass nanocomposites with different coating compositions have been first performed. The measurements were carried out on the laser ablation apparatus created especially for this purpose, in which the YAG–Nd laser pulsed radiation was used. Statistical processing the results of the measurements for all the samples allowed us to obtain the dependences of the threshold parameters of ablative destruction on the physical and chemical properties of nanocoatings, in particular, on the duration of the laser pulse, on the sample transmission, thickness of the coating and the chemical composition of the film-forming solution.

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