

Article

Influence of the Characteristics of Multilayer Interference Antireflection Coatings Based on Nb, Si, and Al Oxides on the Laser-Induced Damage Threshold of ZnGeP₂ Single Crystal

Nikolai Nikolayevich Yudin ^{1,2,3,*}, Mikhail Zinoviev ^{1,2,3} , Vladislav Gladkiy ⁴, Evgeny Moskvichev ¹ , Igor Kinyaevsky ⁵ , Sergey Podzyvalov ^{1,3} , Elena Slyunko ^{1,3}, Elena Zhuravleva ¹, Anastasia Pfaf ¹, Nikolai Aleksandrovich Yudin ^{1,2} and Maxim Kulesh ^{1,*}

- ¹ Laboratory for Radiophysical and Optical Methods of Environmental Studies, National Research Tomsk State University, 634050 Tomsk, Russia; muxa9229@gmail.com (M.Z.); em_tsu@mail.ru (E.M.); cginen@yandex.ru (S.P.); elenohka266@mail.ru (E.S.); lenazhura@mail.ru (E.Z.); nastya.pfayff17@mail.ru (A.P.); yudin@tic.tsu.ru (N.A.Y.)
- ² Laboratory of Remote Sensing of the Environment, V.E. Zuev Institute of Atmospheric Optics SB RAS, 634055 Tomsk, Russia
- ³ Department of Optical Measurements, LOC LLC, 634050 Tomsk, Russia
- ⁴ STC IZOVAC, 220075 Minsk, Belarus; info@izovac.com
- ⁵ Laboratory of Gas Lasers, P.N. Lebedev Institute of Physics RAS, 119333 Moscow, Russia; kinyaevskiyio@lebedev.ru
- * Correspondence: rach3@yandex.ru (N.N.Y.); kyleschMM2000@yandex.ru (M.K.); Tel.: +7-996-938-71-32 (N.N.Y.); +7-983-237-90-48 (M.K.)



Citation: Yudin, N.N.; Zinoviev, M.; Gladkiy, V.; Moskvichev, E.; Kinyaevsky, I.; Podzyvalov, S.; Slyunko, E.; Zhuravleva, E.; Pfaf, A.; Yudin, N.A.; et al. Influence of the Characteristics of Multilayer Interference Antireflection Coatings Based on Nb, Si, and Al Oxides on the Laser-Induced Damage Threshold of ZnGeP₂ Single Crystal. *Crystals* **2021**, *11*, 1549. <https://doi.org/10.3390/cryst11121549>

Academic Editors: Xiaoming Duan, Renqin Dou, Linjun Li and Xiaotao Yang

Received: 14 November 2021

Accepted: 8 December 2021

Published: 10 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: In this work, the effect of the defect structure and the parameters of antireflection interference coatings based on alternating layers of Nb₂O₅/Al₂O₃ and Nb₂O₅/SiO₂ layers on the laser-induced damage threshold of ZGP crystals under the action of Ho:YAG laser radiation at a wavelength of 2.097 μm was determined. Coating deposition was carried out using the ion-beam sputtering method. The laser-induced damage threshold of the sample with a coating based on alternating layers Nb₂O₅ and SiO₂ was W_{0d} = 1.8 J/cm². The laser-induced damage threshold of the coated sample based on alternating layers of Nb₂O₅ and Al₂O₃ was W_{0d} = 2.35 J/cm². It has been found that the presence of silicon conglomerates in an interference antireflection coating leads to a decrease in the laser-induced damage threshold of a nonlinear crystal due to local mechanical stresses and the scattering of incident laser radiation.

Keywords: laser-induced damage threshold; ZnGeP₂; interference coating

1. Introduction

Increasing the power and efficiency of mid-IR laser systems remains one of the main problems of modern laser physics and technology, which is conditioned upon the need for such systems when solving many scientific and applied tasks. Such tasks include remote gas analysis and the monitoring of the atmosphere [1], material processing [2], the investigation of new physical effects [3], generation of attosecond X-ray pulses and particle acceleration [4], and many others. One of the main methods of producing high-power laser radiation in the mid-IR range is the parametric frequency conversion of near-IR lasers [5,6] using nonlinear optical crystals. One of the most effective crystals for this task in the wavelength range of 3–5 μm is a single crystal ZnGeP₂ (ZGP) [6,7], which is sometimes called the “standard” of nonlinear crystals in the mid-IR range [6]. ZGP is a nonlinear positive (n_e > n_o) uniaxial crystal with a crystalline lattice of the Chalcopyrite type [8,9]. ZGP has a high value of nonlinear susceptibility of 75 × 10^{−12} m/V and a thermal conductivity of 36 W/(m × K), as compared to other nonlinear crystals [8,9]. However, a high refractive index of ~3 and, consequently, a high degree of pump radiation reflection

at the crystal–air interface significantly reduce the efficiency of nonlinear conversion in the crystal. To increase this significantly, it is necessary to apply antireflection coatings on the working surfaces of the crystal in the required conversion range. Strict requirements on the value of optical strength are imposed for such coatings, which, at least, should not be lower than the optical strength of the crystal itself. It should be noted that a reliable long-term operation of powerful nonlinear ZGP-based converters is limited by the optical breakdown effect [3–6]. In this regard, the potential for the practical use of high-power parametric oscillators in the mid-IR range while pumping by radiation in the wavelength range of $\sim 2.1\text{ }\mu\text{m}$ is associated with the need to determine technological factors affecting the laser-induced damage threshold (LIDT). The problem of ZGP optical breakdown by laser radiation at wavelengths from $1.064\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$ has been discussed in several previously published works [10–16]. These studies revealed a significant difference in the value of the LIDT of the ZGP crystal at wavelengths of 1064 nm and 2100 nm [10]. A dynamic visualization of the breakdown process by laser radiation at a wavelength of 2100 nm in the ZGP volume showed that an avalanche-like increase in temperature occurs in the forming track inside the nonlinear optical element [11]. An increase in the ZGP breakdown threshold reported in [12] with a decrease in the pump pulse duration “testifies in favor of the thermal nature of breakdown for nanosecond pulses due to anomalous infrared absorption”. It was shown in [15] that when the crystal is cooled to a temperature of $-60\text{ }^{\circ}\text{C}$, the LIDT increases by three times up to 9 J/cm^2 at a wavelength of the acting laser radiation of $2.091\text{ }\mu\text{m}$ and a pulse repetition rate of 10 kHz .

In [13], it was reported that the LIDT of ZGP elements at a wavelength of $9.55\text{ }\mu\text{m}$ was determined from the intensity of the incident beam of 142 MW/cm^2 with a pulse duration of 85 ns and a pulse repetition rate of 1 Hz , which is $\sim 9.5\text{ J/cm}^2$ by the pulse energy density. It was also reported in these works that the threshold for the laser destruction of the ZGP surface is associated with the level of the energy density of the pump radiation rather than the radiation intensity [14]. The direct dependence of the LIDT on the growth technology and the optical quality of crystals was demonstrated in [15]. In [16], it was shown that improving the polishing of working surfaces and reducing or completely removing the near-surface fractured layer leads to an increase in the breakdown threshold. It was shown in [17] that the threshold values of laser damage measured for samples with an antireflection coating are significantly lower than for samples without a coating. At the same time, it was shown in [16] that the deposition of antireflection interference coatings leads to a twofold increase in the LIDT. In [17], it is directly concluded that further research should be focused on improving the quality of the antireflection coating using a high-quality ZGP crystal in order to increase the output power and the efficiency of parametric conversion in a ZGP crystal in the spectral range of $3\text{--}5\text{ }\mu\text{m}$. Thus, the large scatter in the values of the LIDT of the ZGP crystal and the difference in interpretations of the results of studies given in previous works show that physical mechanisms of this negative effect and its dependence—in particular, the technology of deposition of interference coatings—remain not fully understood.

Currently, there are many film-forming materials that can cover a wide range from UV to mid-IR. Several materials, such as Ta_2O_5 , Nb_2O_5 , SiO_2 , HfO_2 , YbF_3 , ZnS , Al_2O_3 , etc., have high transparency and low absorption coefficients in the mid-IR region of the spectrum from 2 to $13\text{ }\mu\text{m}$ [18–22]. These materials are being actively studied and are the most promising as film-forming materials for the development of antireflection coatings and dielectric mirrors with high radiation resistance. Thus, in [18], a dielectric mirror was produced on a fused silica substrate with a radiation strength of about 42 J/cm^2 , which is practically commensurate with the strength of the substrate itself. In [19], the effect of the substrate temperature during the deposition of a film-forming material was investigated, and the dependence of the LIDT of the coating depending on the deposition conditions was shown. The authors of [20,21] also show differences in the strength of the produced dielectric coatings depending on the conditions of material deposition. However, most of these studies were carried out using quartz, sapphire substrates, and similar optical

windows that are transparent in the mid-IR range. There is practically no information related to the study of the mentioned materials deposited using the method of ion-beam sputtering on crystalline materials of the ZGP type. Thus, it is necessary to study the influence of the deposition parameters of the material and the choice of the material on the optical strength of these coatings.

The contradictory information on the influence of interference coatings on the LIDT of ZGP presented in [16,17] indicates that the different structures of coatings and methods of their deposition on a nonlinear crystal, as well as the choice of the film-forming materials, significantly affects the efficiency of its application in optical parametric oscillators.

The aim of the studies presented in this work is to determine the effect of the defect structure and parameters of antireflection interference coatings on the LIDT of ZGP crystals under the action of Ho:YAG laser radiation at a wavelength of 2.097 μm (the most common pump source for parametric oscillators of mid-IR light based on crystals ZGP). Two types of coatings were investigated: based on alternating layers of Nb_2O_5 and Al_2O_3 and based on alternating layers of Nb_2O_5 SiO_2 layers. Coating deposition was carried out using the ion-beam sputtering method.

2. ZGP Substrates (Manufactured by LLC “LOC”, Tomsk, Russia) and Their Parameters

Three samples of a ZGP single crystal were used for studies of the optical breakdown: samples with dimensions of $6 \times 6 \times 20 \text{ mm}^3$ were cut from a single crystal ZGP boule (manufactured by LLC “LOC”, Tomsk, Russia) at the angles of $\theta = 54.5^\circ$ and $\varphi = 0^\circ$ relative to the optical axis. A single crystal ZnGeP_2 boule was grown using the Bridgman method in the vertical direction on an oriented seed; the growth was carried out from a molten polycrystalline compound previously synthesized using the two-temperature method [15].

One sample was tested without applying an antireflection coating (for convenience, hereinafter referred to as ZGP_clean), the second sample was coated with an antireflection coating based on alternating $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ layers (for convenience, hereinafter referred to as ZGP_ Al_2O_3), the third sample was coated with an antireflection coating based on six alternating layers of $\text{Nb}_2\text{O}_5/\text{SiO}_2$ (for convenience, referred to as ZGP_1_ SiO_2 hereafter), and the fourth sample was coated with an antireflection coating based on four layers of $\text{Nb}_2\text{O}_5/\text{SiO}_2$ (for convenience, referred to ZGP_2_ SiO_2 hereafter).

The absorption of radiation at a wavelength of 2.097 μm for sample ZGP_clean was 0.029 cm^{-1} , for sample ZGP_ Al_2O_3 was 0.03 cm^{-1} , for sample ZGP_1_ SiO_2 was 0.028 cm^{-1} , and for sample ZGP_2_ SiO_2 was 0.029 cm^{-1} .

The phase composition of the samples under study was determined prior to the study using X-ray diffraction analysis. According to the result of X-ray structural analysis, no foreign phases were detected in all the samples under study (Table 1).

Table 1. Results of X-ray diffraction analysis of the samples under study.

Sample	Detected Phases	Phase Content, Mass %	Lattice Parameters, Å
ZGP_clean	ZnGeP_2	100	$a = 5.4706$ $c = 10.7054$
ZGP_ Al_2O_3	ZnGeP_2	100	$a = 5.4707$ $c = 10.7056$
ZGP_1_ SiO_2	ZnGeP_2	100	$a = 5.4707$ $c = 10.7053$
ZGP_2_ SiO_2	ZnGeP_2	100	$a = 5.4706$ $c = 10.7055$

Holograms of the internal volume of the samples under study were obtained using a digital holographic camera DHC-1.064, manufactured by LLC “LOC”. The reconstruction of the produced digital holograms was carried out in order to characterize volumetric

defects. The limiting resolution of the method was $3\ \mu\text{m}$ (a detailed description of the digital holography technique, including those applied to visualization of defects in ZGP and a description of the holographic camera used, is given in [22]). No volume defects were detected in all three samples used in this work.

The working surfaces of the test samples were polished on a 4-PD-200 polishing-and-lapping machine. The initial treatment of the working surfaces of all samples consisted of polishing on a cambric polishing pad using ACM 0.5/0 synthetic diamond powder (average grain size of 270 nm). The amount of material removed was $\sim 50\ \mu\text{m}$, which allowed the fractured layer formed in the process of cutting the crystal into oriented plates and their preliminary grinding to be removed. Then, the samples were additionally polished on a cambric polishing pad using ACM 0.25/0 synthetic diamond powder. After that, the samples were polished on a resin polishing pad made of polishing resin using ACM 0.25/0 synthetic diamond powder. The control of the profile of the working surfaces of the samples under study before the deposition of interference coatings was carried out using a ZYGO NewView 7300 profilometer, which operates on the basis of white light interferometry (Figure 1). Surface areas with a size of $110\ \mu\text{m} \times 110\ \mu\text{m}$ were investigated for each experimental sample, and the following parameters were assessed: the maximum difference in the height and the depth of irregularities on the surface (PV) and root mean square depth of roughness (RMS). These were as follows: for sample ZGP_clean, PV = 31.372 nm, RMS = 0.442 nm; for sample ZGP_Al₂O₃, PV = 34.67 nm, RMS = 0.48 nm; for sample ZGP_1_SiO₂, PV = 39.467 nm, RMS = 0.44 nm; and for sample ZGP_2_SiO₂, PV = 33.871 nm, RMS = 0.46 nm. Figure 1 shows an image of the surface of sample ZGP_clean as an example, produced using a ZYGO NewView 7300 profilometer. As can be seen from Figure 1, the polished surfaces of the samples have a low roughness, but they contain “cavities” whose depth reaches several tens of nm. We assume that these surface defects are not caused by the polishing process but are caused by the emergence of bulk defects of the ZGP crystal itself on the surface; for example, these defects can be caused by dislocations.

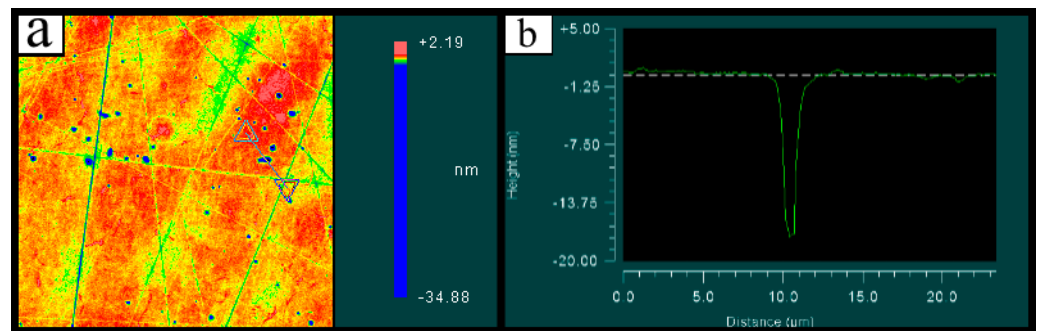


Figure 1. Surface profile of the studied ZGP samples, (a) color diagram of surface roughness, (b) deviations from the average roughness profile along the line (marked with triangles in (a)).

3. Parameters of Interference Coatings Deposition on ZGP Substrates and Their Characteristics

In our work, we used the method of ion-beam sputtering (IBS) of a pure material target with the supply of a reactive gas (oxygen) through a sputtering source. The deposition of dielectric layers was carried out on an Aspira-200 vacuum deposition machine (manufactured by Izovak, Belarus). The sputtered targets were disks of pure material, Si with a purity of 99.999 (5N), Nb with a purity of 99.95 (3N), and Al with a purity of 99.999 (5N). The diameter of each sputtered target was 101.6 mm, and the thickness of the target disk was 6 mm. The targets were fixed on a water-cooled rotary base. The positive charge on the target generated by the ion beam was compensated by the thermal emission of electrons with a hot tungsten cathode. The working gases in the system were gaseous

argon (Ar) with a high purity of 99.995% and technical gaseous oxygen (O₂) with a purity of 99.7%.

Before the deposition process, the substrates were preliminarily cleaned from all kinds of dirt and dust on the surface. Cleaning was carried out using phosphoric acid followed by rinsing with high purity acetone. Immediately before coating in a vacuum chamber, the substrates were additionally cleaned with an auxiliary ion source at a source power of about 100 W and an ion energy of about 600 eV for 3 min.

A preliminary evacuation of the vacuum chamber before the beginning of the spraying process was carried out to values of $5 \cdot 10^{-4}$ Pa using a turbomolecular pump. The working residual pressure in the chamber during layer deposition was as follows: for the Nb₂O₅ layer, it was $5 \cdot 10^{-2}$ Pa; for the SiO₂ layer, it was $3.9 \cdot 10^{-2}$ Pa; and for the Al₂O₃ layer, it was $4.8 \cdot 10^{-2}$ Pa. The average deposition rate of the layers was 0.75 Å/s for Nb₂O₅, 2 Å/s for the SiO₂ layer, and 0.85 Å/s for the Al₂O₃ layer.

The primary step for the development and deposition of an interference antireflection coating is to obtain information on the dispersion of the refractive index and absorption in the monolayers from which this coating will be constructed. Thus, we have carried out studies to obtain the optical characteristics of the films of these materials. The thickness of the monolayers was about 1 µm for their correct description in the IR and visible spectral regions. The deposition thickness control was single-wavelength and optical, with a selected wavelength of 550 nm. The monolayers were deposited on pure silicon substrates (refractive index ~3.4) and Asahi optical glass.

After deposition, the monolayers were measured for transmission and reflection on a Shimadzu UV-3600 Plus spectrophotometer (operating wavelength range 180–3300 nm) and a Simex FTIR spectrometer. A typical transmission spectrum of a monolayer is shown in Figure 2 (measurements carried out for Al₂O₃).

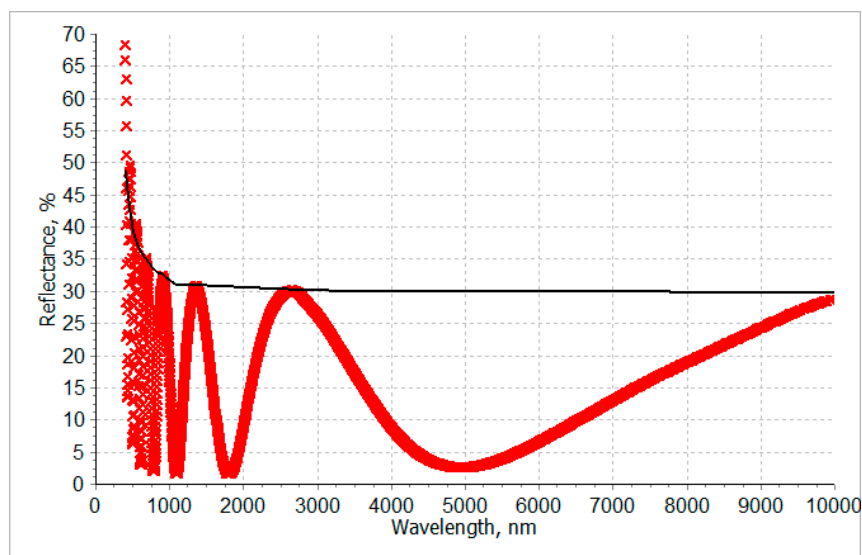


Figure 2. Transmission spectrum of a Al₂O₃ monolayer with a thickness of 1 µm deposited onto a substrate of Asahi optical glass.

The calculation of the dependence of the refractive index and the absorption coefficient on the wavelength of the monolayer was carried out using the Optilayer software and the built-in Optichar module. The obtained dispersions of the refractive index of the monolayers, as well as the dimensionless absorption coefficient, are shown in Figure 3.

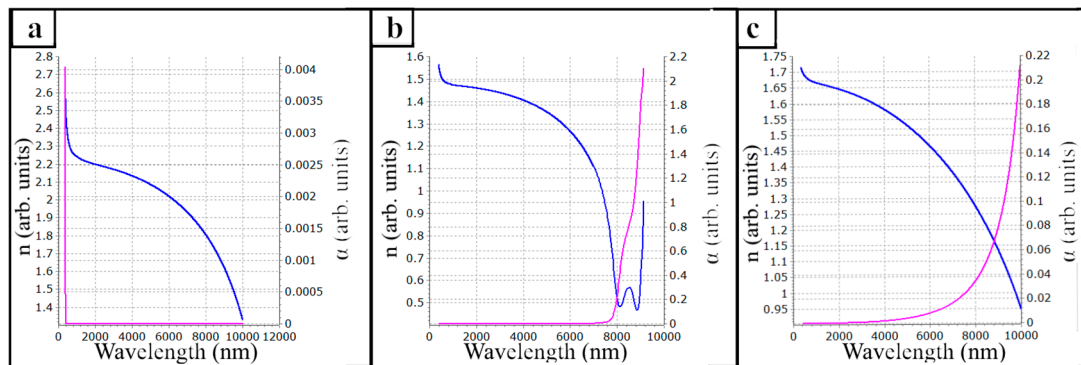


Figure 3. Calculated Optilayer dependences of the refractive index and the absorption coefficient on the wavelength: (a) Nb_2O_5 monolayer, (b) SiO_2 monolayer, (c) Al_2O_3 monolayer.

The obtained dependences of the change in the refractive index and the absorption coefficient on the wavelength showed that all the monolayers under study are transparent in the required range, and the absorption in these layers is insignificant (in the case of Al_2O_3) or is completely absent (as in the case of the Nb_2O_5 and SiO_2 layers). As can be seen from the obtained dispersions, the Al_2O_3 and SiO_2 layers have resonant absorption lines with a sharp jump-like change in the refractive index. For the SiO_2 layer, it begins at a wavelength of $\sim 8 \mu\text{m}$ and has a steeper rise in the absorption curve, while the Al_2O_3 layer demonstrates a gentler increase in the absorption coefficient with a maximum in the region of $10\text{--}12 \mu\text{m}$. However, both films have insignificant absorption in the required wavelength range ($25 \mu\text{m}$) and are suitable as materials for the development of AR coatings. The refractive indices of the produced films are close to the values obtained by the authors of other works. Thus, the refractive index at a wavelength of 550 nm of the Nb_2O_5 film was 2.34 , for SiO_2 was 1.47 , and for Al_2O_3 was 1.68 . According to the literature data, such indicators are typical for stoichiometric close-packed films without significant defects and a porous structure.

Thus, the calculated dispersions of the refractive index and the absorption coefficient of the monolayers under study were subsequently used to design two different AR coatings based on pairs of layers $\text{Nb}_2\text{O}_5/\text{SiO}_2$ and $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$. The development of the coatings was carried out using the Optichar software. The sprayed coating was inspected using an Asahi optical glass witness at a wavelength of 550 nm .

An antireflection coating was not applied to sample ZGP_clean. Sample ZGP_ Al_2O_3 was coated with a four-layer antireflection coating based on compounds Nb_2O_5 (high refractive layer) and Al_2O_3 (low refractive layer) with a thickness of 2133 nm . Sample ZGP_1_ SiO_2 was coated with a six-layer antireflection coating based on alternating layers of Nb_2O_5 and SiO_2 compounds with a total thickness of $\sim 2900 \text{ nm}$. Sample ZGP_2_ SiO_2 was coated with a four-layer antireflection coating based on alternating layers of Nb_2O_5 and SiO_2 compounds with a total thickness of $\sim 700 \text{ nm}$. Figure 4 shows the reflection spectra of samples ZGP_ Al_2O_3 , ZGP_1_ SiO_2 and ZGP_2_ SiO_2 with applied interference coatings, obtained using a Simex Fourier spectrometer. The morphology of interference coatings and the composition of the samples under study were analyzed using a scanning electron microscope with a Tescan MIRA 3 LMU Schottky cathode (TESCAN ORSAY HOLDING, Brno, Czech Republic) equipped with an Oxford Instruments Ultim Max 40 energy dispersive X-ray spectrometer (Oxford Instruments, High Wycombe, UK). Scanning was performed at an accelerating voltage (HV) of 20 kV . The samples were coated with a carbon-conductive coating in a Quorum Technologies EMITECH K450X setup (Quorum Technologies, Laughton, UK). As studies have shown, silicon conglomerates of submicron size 3 were found in sample ZGP_1_ SiO_2 in the layers of the interference coating (Figure 5b). No defects in the interference antireflection coating were found in sample ZGP_ Al_2O_3 .

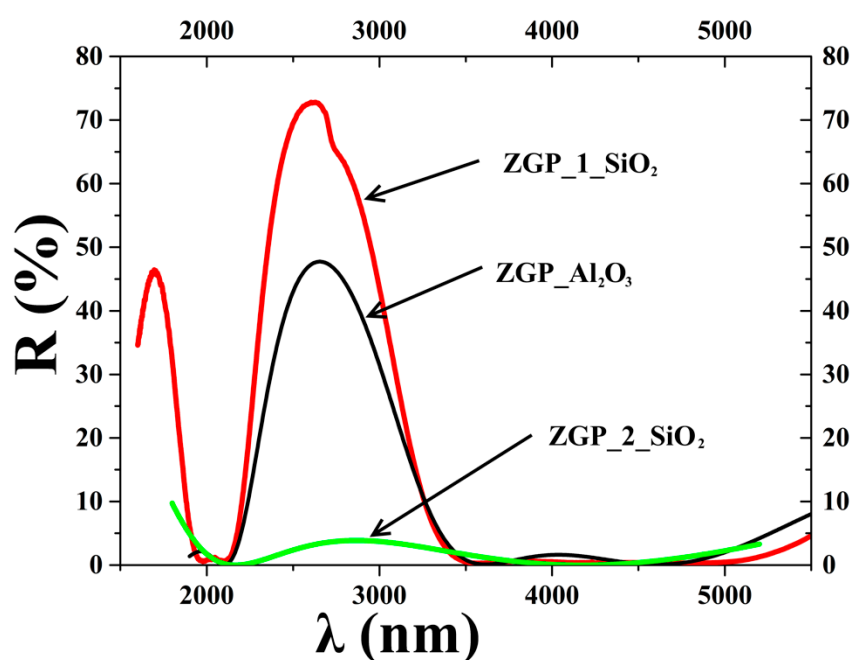


Figure 4. Reflection spectra of working faces of samples ZGP_Al₂O₃, ZGP_1_SiO₂ and ZGP_2_SiO₂ with applied interference coatings.

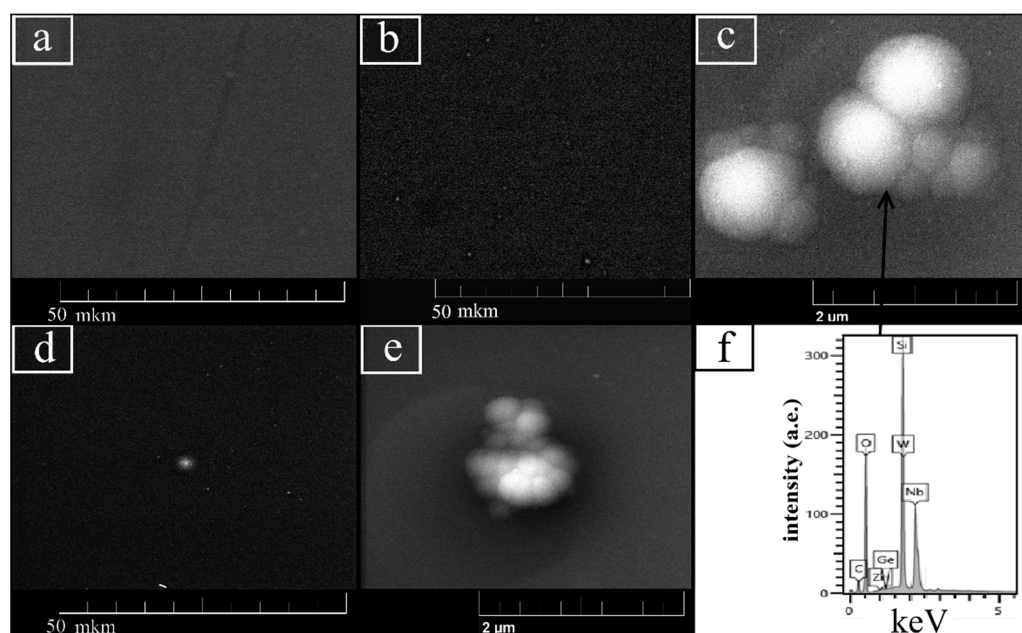


Figure 5. Morphology of interference coatings of samples under study were analyzed using a scanning electron microscope with a Tescan MIRA 3 LMU Schottky cathode equipped with an Oxford Instruments Ultim Max 40 energy dispersive X-ray spectrometer and the chemical composition of the local area of the ZGP_1_SiO₂ sample near silicon conglomerates: (a) image of the surface of the interference coating of sample ZGP_Al₂O₃; (b) image of the surface of the interference coating of sample ZGP_1_SiO₂; (c) enlarged image of the silicon conglomerate of the coating sample ZGP_1_SiO₂; (d) image of the surface of the interference coating of sample ZGP_2_SiO₂; (e) enlarged image of the silicon conglomerate of the coating sample ZGP_2_SiO₂; (f) chemical composition of the coating sample ZGP_1_SiO₂.

4. Setup Parameters and Technique for Determining the LIDT of the Samples under Study

A Ho:YAG laser generating radiation at a wavelength of $2.097\ \mu\text{m}$ pumped by a cw thulium fiber was the source of radiation. The Ho:YAG laser operated in the active Q-switched mode with a pulse duration $\tau = 35\ \text{ns}$ and a pulse repetition rate of $10\ \text{kHz}$. The measured diameter in all experiments was $d = 350 \pm 10\ \mu\text{m}$ at the e^{-2} level of the maximum intensity. The maximum average radiation power generated by the Ho:YAG laser was $20\ \text{W}$ in a linearly polarized Gaussian beam (parameter $M^2 \leq 1.3$).

The schematic layout of the experimental stand is shown in Figure 6. The power of the incident laser radiation was changed using an attenuator consisting of a half-wave plate ($\lambda/2$) and a polarizing mirror (M1). A Faraday isolator (F.I.) was used to prevent the reflected radiation from entering the laser, which prevented an uncontrolled change in the parameters of the incident radiation. The average laser power (P_{av}) was measured before each experiment with an Ophir power meter (P.M.).

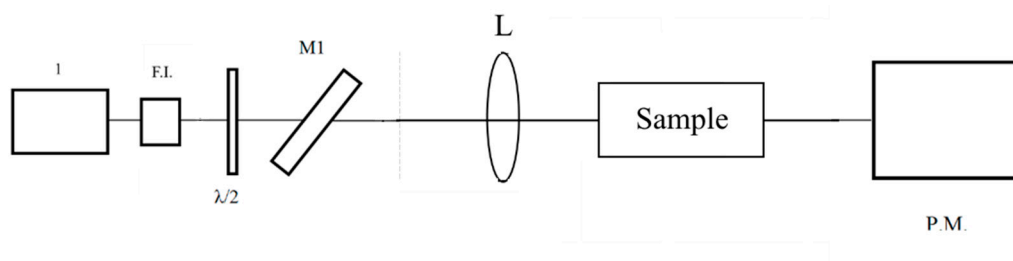


Figure 6. Optical schematic layout of the experimental setup: 1 is the Ho:YAG laser, F.I. is the Faraday isolator, $\lambda/2$ is the half-wave plate, M1 is the polarizing mirror, L is the lens, P.M. is the Ophir power meter.

According to the international standard ISO11146 [23], the energy density of laser radiation was determined by the following expression:

$$W = 8 P_{\text{av}} / (f\pi d^2), \quad (1)$$

where d is the diameter of the laser beam.

The “R-on-1” technique was used to determine the LIDT of the samples, which requires less space on the sample surface compared to the “S-on-1” technique and, therefore, can be used for samples with a limited aperture; however, it is considered coarser [24]. The essence of this technique is that each individual region of the crystal is irradiated with laser radiation with a sequential increase in the intensity of the laser radiation until an optical breakdown occurs or a predetermined value of the energy density is reached. In our work, the study was carried out with an exposure duration $\tau_{\text{ex}} = 5\ \text{s}$. The sample under study was exposed to packets of laser pulses with a fixed energy density level, which did not cause damage to the crystal surface. Then, the energy density level was increased with a step of $\sim 0.1\ \text{J}/\text{cm}^2$. The experiment was terminated when visible damage appeared on one of the surfaces of the nonlinear element. Then, the sample was moved $0.5\ \text{mm}$ in height or width using a two-dimensional movement; the experiment was repeated five times. The optical breakdown probability was obtained by plotting the cumulative probability versus the optical breakdown energy density. The value of the LIDT (W_{0d}) was taken to be the energy density corresponding to the approximation of the optical breakdown probability to zero. Figure 7 shows the results of measuring the LIDT using the R-on-1 technique. In the presented plots, the ordinate represents the probability of optical breakdown in relative units, normalized to unity, and the abscissa represents the energy density of the testing laser radiation.

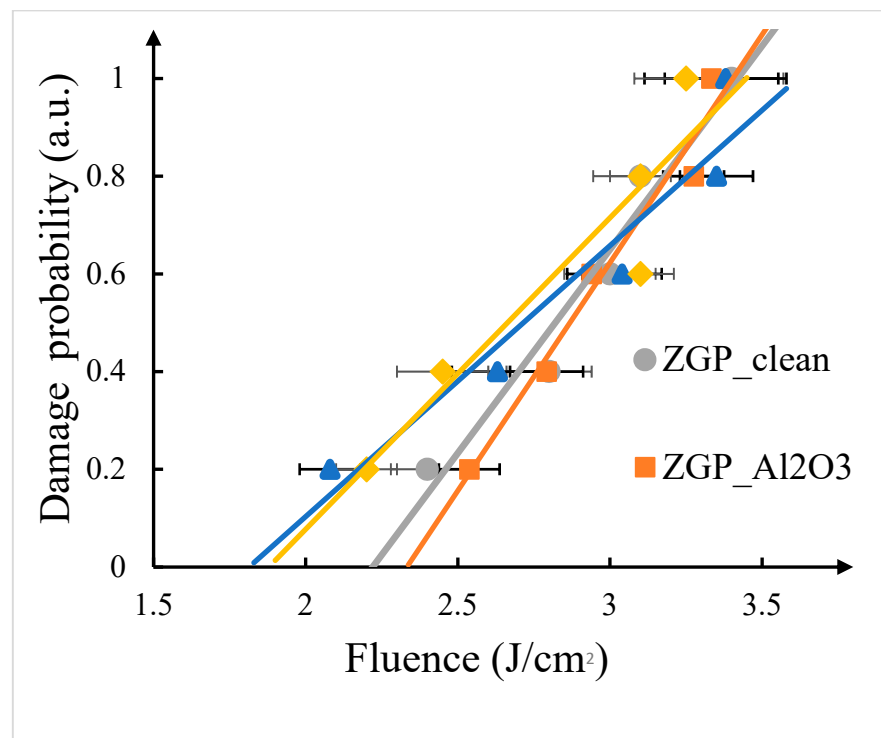


Figure 7. Dependence of the optical breakdown probability of samples ZGP_clean, ZGP_Al₂O₃ and ZGP_1_SiO₂, ZGP_2_SiO₂ on the energy density of the incident laser radiation.

5. Experimental Results and Their Discussion

The LIDT values for samples ZGP_clean (without antireflection coatings), ZGP_Al₂O₃ (with a coating based on alternating layers of Nb₂O₅ and Al₂O₃), ZGP_1_SiO₂, and ZGP_2_SiO₂ (with a coating based on alternating layers of Nb₂O₅ and SiO₂) (Figure 7) were determined according to the R-on-1 technique, using the experimental stand shown in Figure 6.

Thus, the LIDT for sample ZGP_clean (without antireflection coatings) was $W_{0d} = 2.23 \text{ J/cm}^2$. The LIDT for sample ZGP_Al₂O₃ (coated with alternating layers Nb₂O₅ and Al₂O₃) was $W_{0d} = 2.35 \text{ J/cm}^2$. The LIDT for sample ZGP_1_SiO₂ (coated with alternating layers Nb₂O₅ and SiO₂) was $W_{0d} = 1.8 \text{ J/cm}^2$. The LIDT for sample ZGP_2_SiO₂ (coated with alternating layers Nb₂O₅ and SiO₂) was $W_{0d} = 1.86 \text{ J/cm}^2$. All the samples under study had low absorption at the wavelength of exposure, which indicates a low concentration of point defects that affect the absorption intensity. The presence of binary phosphides and impurity elements and bulk defects was not detected in all the samples under study, which indicates a good quality of the crystal structure of the single crystal.

In previous studies, other researchers have shown that a decrease in the number of layers of the interference coating and the film thickness has a positive effect on the LIDT of the sample surface [21,25]. Moreover, coatings based on SiO₂ showed high LIDT values for various substrate materials compared to coatings based on Al₂O₃ [25]. As can be seen from the results of our experiments, the difference in the thickness of the coatings and in the number of layers in the antireflection coating based on alternating Nb₂O₃/SiO₂ layers is not significant for LIDT. The results in Figure 7 show that a decrease in the coating thickness and a decrease in the number of layers based on the alternation of Nb₂O₃/SiO₂ materials did not lead to a change in LIDT (the antireflection coating of the ZGP_1_SiO₂ sample is four times thicker than the ZGP_2_SiO₂ sample, and the number of layers is smaller). In our works, we also reduced the rate of the silicon target sputtering. A twofold decrease in the velocity, to 1–1.2 A/s, did not show a significant change in the radiation resistance parameter of the finished coating based on the pair of Nb₂O₃/SiO₂ materials. However, it should be noted that the rate reduction was achieved by changing the anode voltage

at the spraying source without changing the gas supply mode. The results obtained on antireflection coatings based on alternating $\text{Nb}_2\text{O}_3/\text{SiO}_2$ layers can be explained by the lack of oxygen during the deposition of SiO_2 layers, which leads to the incomplete oxidation of the ZGP material deposited on the surface of the samples and the presence of silicon islands in the formed film. This circumstance is most likely the reason for the lower LIDT value compared to the uncoated sample and the absence of the LIDT dependence on the film thickness. This statement is confirmed by the results presented in Figure 5f (according to the chemical formula, SiO_2 , the intensity of the spectral lines of the corresponding to O should be higher than the intensity of the spectral lines of silicon (Si), but the opposite picture is actually observed). It is planned to conduct a series of experiments with a change in the gas mode with an increased oxygen content in the plasma to further improve the optical stability of the $\text{Nb}_2\text{O}_3/\text{SiO}_2$ coating. Moreover, it is planned to make an attempt to sputter a quartz SiO_2 target in an argon plasma with a low oxygen content instead of a pure silicon target, which, according to literature data [26], can give a better characterization of the stoichiometry of the film composition and, as a consequence, a possible increase in LIDT.

Si conglomerates in samples ZGP_1- SiO_2 and ZGP_2- SiO_2 can be “seed inhomogeneities” for the initialization of the optical breakdown process due to local mechanical stresses and the scattering of laser radiation, which leads to a decrease in the LIDT in comparison with uncoated sample. In turn, the absence of local fluctuations of the composition and mechanical stresses in the case of sample ZGP- Al_2O_3 leads to an increase in the LIDT in comparison with the uncoated sample due to the “closure” of dangling chemical bonds on the polished surface.

Another factor that can affect the difference between LIDT coatings based on $\text{Nb}_2\text{O}_3/\text{SiO}_2$ and $\text{Nb}_2\text{O}_3/\text{Al}_2\text{O}_3$ may be the poor adhesion of films based on SiO_2 to the substrate compared to Al_2O_3 [25]. However, one of the adhesion tests that we can carry out is a peel-off test with an adhesive tape (both coatings pass the test—layers do not peel off) and the annealing of samples at a temperature of $\sim 400^\circ\text{C}$ in an atmosphere for 1 hour, at which both coatings come off the substrates, cracking and flaking. Thus, in this work, we failed to make a correct comparison of the interlayer adhesion and the adhesion of coatings based on $\text{Nb}_2\text{O}_3/\text{SiO}_2$ and $\text{Nb}_2\text{O}_3/\text{Al}_2\text{O}_3$ to the substrate.

6. Conclusions

Designs of interference coatings based on the alternation of Nb_2O_5 and SiO_2 layers and on the alternation of Nb_2O_5 and Al_2O_3 layers for ZGP single crystals used in parametric light generators generating radiation in the wavelength range of 3–5 μm when pumped by laser radiation at a wavelength of $\sim 2.1 \mu\text{m}$ have been developed during the research. The technology for sputtering these coatings using the ion-beam sputtering method has been developed. The LIDT at a wavelength of the acting laser radiation of 2.097 μm was determined at a pulse repetition rate of 10 kHz and a pulse duration of 35 ns for ZGP single crystals manufactured by LLC “LOC”, which was $W_{0d} = 2.23 \text{ J/cm}^2$ without antireflection coatings. The LIDT of the sample with a coating based on alternating layers Nb_2O_5 and SiO_2 was $W_{0d} = 1.8 \text{ J/cm}^2$. The LIDT of the coated sample based on alternating layers Nb_2O_5 and Al_2O_3 was $W_{0d} = 2.35 \text{ J/cm}^2$.

It has been found that the presence of silicon conglomerates in an interference antireflection coating is a consequence of a lack of oxygen during the deposition of SiO_2 layers, which leads to the incomplete oxidation of the ZGP material deposited on the surface of the samples. It has been found that the presence of silicon conglomerates in an interference antireflection coating leads to a decrease in the LIDT of a nonlinear crystal due to local mechanical stresses and scattering of incident laser radiation, even in the absence of bulk and linear defects of the crystal itself. In turn, the absence of local fluctuations of the composition and mechanical stresses in the case of the sample with a coating based on alternating layers of Nb_2O_5 and Al_2O_3 leads an increase in the LIDT in comparison

with an uncoated sample due to the closure of dangling chemical bonds emerging on the polished surface.

The work has been carried out using the equipment of the Tomsk Regional Research Equipment Sharing Center of TSU.

Author Contributions: Conceptualization, N.N.Y., I.K. and M.Z.; methodology, M.Z.; software, V.G. and M.K.; validation, N.A.Y., N.N.Y. and E.S.; formal analysis, M.K.; investigation, E.M., V.G., M.Z. and S.P.; resources, N.N.Y.; data curation, E.S. and E.Z.; writing—original draft preparation, A.P. and E.S.; writing—review and editing, N.N.Y. and S.P.; visualization, M.K.; supervision, N.N.Y.; project administration, N.N.Y.; funding acquisition, N.N.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Tomsk State University Development Programme («Priority-2030»).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

- Boyd, G.D.; Beuhler, E.; Stortz, F.G. Linear and nonlinear optical properties of ZnGeP₂ and CdSe. *Appl. Phys. Lett.* **1971**, *18*, 301–304. [\[CrossRef\]](#)
- Dmitriev, V.G.; Gurzadyan, G.G.; Nikogosyan, D.N. *Handbook of Nonlinear Optical Crystals*; Springer: New York, NY, USA, 1999; 413p.
- Beasley, J.D. Thermal conductivities of some novel nonlinear optical materials. *Appl. Opt.* **1994**, *33*, 1000–1003. [\[CrossRef\]](#)
- Hemming, A.; Richards, J.; Davidson, A.A.; Carmody, N.; Bennetts, S.; Simakov, N.; Haub, J. 99 W mid-IR operation of a ZGP OPO at 25% duty cycle. *Opt. Express* **2013**, *21*, 10062–10069. [\[CrossRef\]](#) [\[PubMed\]](#)
- Haakestad, M.W.; Fonnum, H.; Lippert, E. Mid-infrared source with 0.2 J pulse energy based on nonlinear conversion of Q-switched pulses in ZnGeP₂. *Opt. Express* **2014**, *22*, 8556–8564. [\[CrossRef\]](#)
- Qian, C.; Yao, B.; Zhao, B.; Liu, G.; Duan, X.; Ju, Y.; Wang, Y. High repetition rate 102 W middle infrared ZnGeP₂ master oscillator power amplifier system with thermal lens compensation. *Opt. Lett.* **2019**, *44*, 715–718. [\[CrossRef\]](#) [\[PubMed\]](#)
- Das, S. Optical parametric oscillator: Status of tunable radiation in mid-IR to IR spectral range based on ZnGeP₂ crystal pumped by solid state lasers. *Opt. Quant. Electron.* **2019**, *51*, 70. [\[CrossRef\]](#)
- Nikogosyan, D. *Nonlinear Optical Crystals: A Complete Survey*; Springer: New York, NY, USA, 2005; 440p.
- Aggarwal, R.L.; Lax, B. *Nonlinear Infrared Generation*; Shen, Y.R., Ed.; Academic: New York, NY, USA, 1977; 28p.
- Hildenbrand, A.; Kieleck, C.; Tyazhev, A.; Marchev, G.; Stöppler, G.; Eichhorn, M.; Schunemann, P.G.; Panyutin, V.L.; Petrov, V. Laser damage of the nonlinear crystals CdSiP₂ and ZnGeP₂ studied with nanosecond pulses at 1064 and 2090 nm. *Opt. Eng.* **2014**, *53*, 122511. [\[CrossRef\]](#)
- Gribenyukov, A.I.; Dyomin, V.V.; Olshukov, A.S.; Podzyvalov, S.N.; Polovcev, I.G.; Yudin, N.N. Investigation of the process of laserinduced damage of ZnGeP₂ crystals using digital holography. *Rus. Phys. J.* **2018**, *61*, 2042–2052. [\[CrossRef\]](#)
- Chumside, J.H.; Wilson, J.J.; Gribenyukov, A.I.; Shubin, S.F.; Dolgii, S.I.; Andreev, Y.u.M.; Zuev, V.V.; Boulder, V. Co:NOAA Technical Memorandum ERL WPL-224 WPL-224wpl; IAP: Potsdam, Germany, 1992; p. 18.
- Andreev Yu, M.; Badikov, V.V.; Voevodin, V.G.; Geiko, L.G.; Geiko, P.P.; Ivashchenko, M.V.; Karapuzikov, A.I.; Sherstov, I.V. Radiation resistance of nonlinear crystals at a wavelength of 9.55 μm. *Quantum Electron.* **2001**, *31*, 1075–1078. [\[CrossRef\]](#)
- Peterson, R.D.; Schepler, K.L.; Brown, J.L.; Schunemann, P.G. Damage properties of ZnGeP₂ at 2 μm. *JOSA B* **1995**, *12*, 2142–2146. [\[CrossRef\]](#)
- Yudin, N.N.; Antipov, O.L.; Gribenyukov, A.I.; Eranov, I.D.; Podzyvalov, S.N.; Zinoviev, M.M.; Voronin, L.A.; Zhuravleva, E.V.; Zykova, M.P. Effect of postgrowth processing technology and laser radiation parameters at wavelengths of 2091 and 1064 nm on the laser-induced damage threshold in ZnGeP₂ single crystal. *Quantum Electron.* **2021**, *51*, 306–316. [\[CrossRef\]](#)
- Zawilski, K.T.; Setzler, S.D.; Schunemann, P.G.; Pollak, T.M. Increasing the laser-induced damage threshold of single-crystal ZnGeP₂. *JOSA B* **2006**, *23*, 2310–2316. [\[CrossRef\]](#)
- Peng, Y.; Wei, X.; Wang, W. Mid-infrared optical parametric oscillator based on ZnGeP₂ pumped by 2-μm laser. *Chin. Opt. Lett.* **2011**, *9*, 061403. [\[CrossRef\]](#)
- Cheng, X.J.; Zhao, Y.; Qiang, Y.; Zhu, Y.; Guo, L.; Shao, J. Comparison of laser-induced damage in Ta₂O₅ and Nb₂O₅ single-layer films and high. *Chin. Opt. Lett.* **2011**, *9*, 013102. [\[CrossRef\]](#)
- Zhang, Y.; Xiong, S.; Huang, W. Study on defects in ZnS/YbF₃ infrared coatings on silicon substrates. *Surf. Coat. Technol.* **2017**, *320*, 3–6. [\[CrossRef\]](#)
- Chen, K.; Hsu, C.; Liu, J.; Liou, Y.; Yang, C. Investigation of Antireflection Nb₂O₅ Thin Films by the Sputtering Method under Different Deposition Parameters. *Micromachines* **2016**, *7*, 151. [\[CrossRef\]](#) [\[PubMed\]](#)

21. Vanyakin, A.V.; Zheleznov, V.I.; Kulevskii, L.A.; Lukashev, A.V.; Morozov, N.P.; Orlov, N.A. Interference optics for lasers and parametric oscillators emitting in the middle-IR range. *Quantum Electron.* **1997**, *24*, 142–144. [[CrossRef](#)]
22. Dyomin, V.; Gribenyukov, A.; Davydova, A.; Zinoviev, M.; Olshukov, A.; Podzyvalov, S.; Polovtsev, I.; Yudin, N. Holography of particles for diagnostics tasks [Invited]. *Appl. Opt.* **2019**, *58*, G300–G310. [[CrossRef](#)] [[PubMed](#)]
23. ISO 11146-1:2005. *Lasers and Laser-Related Equipment—Test Methods for Laser Beam Widths, Divergence Angles and Beam Propagation Ratios*; American National Standards Institute (ANSI): Washington, DC, USA, 2005.
24. “The R-on-1 Test”, Lidaris LIDT Service. 2019. Available online: <http://lidaris.com/laserdamage-testing/> (accessed on 16 November 2020).
25. Gallais, L.; Commandré, M. Laser-induced damage thresholds of bulk and coating optical materials at 1030 nm, 500 fs. *Appl. Opt.* **2013**, *53*, A186–A196. [[CrossRef](#)] [[PubMed](#)]
26. Telesh, E.; Kasinsky, N.; Tomal, V. Coatings formation by ion beam sputtering of dielectric targets. *Bull. Polotsk State Univ. Ser. C Fundam. Sci.* **2012**, *4*, 23–29.