

<https://doi.org/10.15388/vu.thesis.760>

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Formation of Sculptured Thin Films on Crystalline Substrates and Their Investigation in Laser Systems

DOCTORAL DISSERTATION

Technological Sciences,
Material Engineering (T 008)

VILNIUS 2025

The dissertation was prepared between 2019 and 2023 at Optical coatings laboratory of the Center for physical sciences and technology. The research was supported by Research Council of Lithuania.

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www.vu.lt/lt/naujienos/ivykiu-kalendorius

<https://doi.org/10.15388/vu.thesis.760>

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VILNIAUS UNIVERSITETAS
VALSTYBINIS MOKSLINIŲ TYRIMŲ INSTITUTAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

Lukas Ramalis

Skulptūrinių plonų sluoksnių formavimas ant kristalinių padėklų ir jų tyrimai lazerinėse sistemose

DAKTARO DISERTACIJA

Technologijos mokslai,
Medžiagų inžinerija (T 008)

VILNIUS 2025

Disertacija rengta 2019–2023 metais Optinių dangų laboratorijoje, Valstybiniame mokslinių tyrimų institute Fizinių ir technologijos mokslų centre. Mokslinius tyrimus rėmė Lietuvos mokslo taryba.

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Disertacija ginama viešame Gynimo tarybos posėdyje 2025 m. gegužės mėn. 28 d. 14 val. FTMC Fizikos instituto salėje.

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Disertaciją galima peržiūrėti Fizinių ir technologijos mokslų centro, Vilniaus universiteto bibliotekose ir VU interneto svetainėje adresu:

<https://www.vu.lt/naujienos/ivykiu-kalendorius>

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List of abbreviations

PVD	Physical Vapor Deposition
EBD	Electron Beam Deposition
GLAD	GLancing Angle Deposition
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscopy
LIDT	Laser-Induced Damage Threshold
LID	Laser-Induced Deflection
FS	Fused Silica
AR	Anti-Reflective
HR	High-Reflective
QWOT	Quarter Wavelength Optical Thickness
LLIA	Local Laser Irradiation Annealing
AOI	Angle Of Incidence

INTRODUCTION

An era of lasers began on the May 16th, 1960 [1] when Theodore Maiman demonstrated the first laser. His setup consisted of a ruby rod coated with silver on its surfaces, exposed to a high-power flash lamp to produce laser radiation. Shortly after, Paul D. Maker and colleagues [2] observed the first instance of laser-induced damage in dielectric films, as reported in their groundbreaking work. This discovery opened a new field of studies focused on the development and optimization of optical coatings.

During the laser systems development the need for advanced optical coatings also grew. Techniques such as physical vapor deposition (PVD) [3] and chemical vapor deposition (CVD) [4] emerged, enabling the fabrication of increasingly complex and precise optical elements. The continuous enhancement of laser intensity and the reduction in pulse durations have driven demands for coatings with higher performance and reliability. The evolution of laser systems had a huge impact on many other fields of research, telecommunications, medicine, high-tech industry and others.

Despite significant advancements, the optical elements in laser systems – such as anti-reflection (AR) coatings, mirrors, polarizers etc. remain a limiting factor in achieving further improvements. Modern deposition techniques now allow for the production of optical elements with exceptional sub-nm thickness precision, low absorption and stable refractive indices [5], [6]. Standard configuration using alternating high- and low-refractive-index materials provide the necessary optical properties. However, the high-refractive-index materials typically have lower band gap energy values, which reduce their resistance to laser radiation [7]. An innovative approach is needed in order to apply laser systems in everyday life more as the laser system dimensions are reduced by replacing existing optical components with more compact. A unique solution is proposed to form multilayer coating directly on existing elements in the microlaser systems (nonlinear crystals).

The glancing angle deposition (GLAD) method presents a promising approach to address these challenges [8]. By adjusting the substrate tilt in terms of vapor flux during deposition process, GLAD enables control over the effective refractive index of materials. This allows for the creation of multilayer structures using only a single material, with refractive index contrast achieved through substrate deposition geometry manipulation. Such versatility facilitates the fabrication of AR coatings, high-reflection (HR) mirrors and other optical elements [8], [9]. Moreover, combining standard and nanostructured layers can further enhance the optical performance of existing components, making them more suitable for modern laser systems [10].

The ability to engineer coatings with modified inner structure and effective refractive indices opens new technological possibilities for optical element design. A notable example is the application of nanostructured coatings to enhance total internal reflection (TIR) in YAG crystals, a critical component for zigzag cavity architectures in slab laser systems. These advanced coatings extend the range of the TIR phenomenon, enabling robust and efficient laser operations. However, challenges such as refractive index instability and environmental degradation – caused by humidity or the absorption of harmful particles – must be addressed.

This thesis explores the design, fabrication and characterization of nanostructured coatings with a focus on their optical properties and durability. Firstly, various materials are analyzed to understand their potential for high-performance coatings. Secondly, fabrication techniques of all-silica mirrors and strategies how to prevent degradation, including environmental stabilization and annealing, are investigated. Thirdly, nanostructured coatings are deposited directly on YAG crystals and investigated. Unique designs are developed to induce the TIR phenomenon, demonstrating the feasibility of these coatings for zig-zag cavity architectures in slab laser systems. By addressing the technical and environmental challenges of nanostructured coatings, this research aims to contribute to the development of more robust and efficient optical elements for next-generation laser systems.

The objective of the thesis

To investigate nanostructured layers optical stability and to extend the applications area of sculptured thin films by manufacturing optical elements directly on YAG laser crystals.

The scientific tasks of the thesis

1. To investigate the effect of deposition angles on the porosity and refractive indices of different materials and determine the correlation between porosity and laser-induced damage threshold.
2. To investigate the formation and stability of all-silica multilayer coatings.
3. To analyze the impact of environmental factors on the optical properties of all-silica mirrors and explore methods to enhance the optical performance and durability.
4. To fabricate all-silica coatings directly on laser crystals and analyze optical performance and environmental stability.

5. To develop a method of depositing multilayer coating on YAG crystal in order to induce total internal reflection.

Scientific novelty and practical value

Nanostructured coatings are widely researched and demonstrated a huge potential for optical element formation. In this dissertation, fabrication of materials with different inner structures are analyzed more in depth. The main aim of this work is to open new possibilities to use sculptured thin films on laser crystals in order to improve existing laser systems. Specifically, scientific novelty and practical value of this dissertation can be summarized in following statements:

- This research provides the first comprehensive investigation of laser-induced damage threshold across multiple materials (Nb_2O_5 , Al_2O_3 , Ta_2O_5 and SiO_2) deposited using glancing angle deposition method. Our findings provide a foundation for future studies on damage mechanisms in nanostructured porous optical coatings.
- All-silica mirrors were investigated in different environments in order to avoid degradation effect. While all-silica mirrors are initially sensitive to environmental conditions, strategic treatment methods can effectively stabilize their optical properties. The most promising environment to avoid degradation consisted of nitrogen or argon gases.
- Local laser radiation annealing was applied to all-silica mirrors. This method has resulted in unprecedented laser-induced damage threshold values, indicating the potential of all-silica mirrors to withstand extreme laser fluence (180 J/cm^2 at 355 nm wavelength in nanosecond regime). This breakthrough positions such coatings as a viable solution for high-power laser applications.
- Nanostructured SiO_2 coatings were fabricated on YAG crystal and investigated. Produced Bragg mirror coatings at 532 nm wavelength exhibit high laser-induced damage threshold ($>140 \text{ J/cm}^2$) using nanosecond regime pulsed laser.
- The research presented in this work demonstrates a novel approach to improve the performance of YAG crystals in laser system by using nanostructured coatings. The applied GLAD methods show the

potential for expanding total internal reflectance angular range from 55° to 46° in YAG prisms by for the first time implementing unique TIR-interference SiO₂ coating nanostructured-sculptured layers.

Statements to defend

1. LIDT values of columnar nanostructured Nb₂O₅, Al₂O₃, Ta₂O₅ and SiO₂ deposited using GLAD method are more influenced by defects than by the porosity in single layers.
2. The degradation of optical performance of multilayer all-silica mirrors can be suppressed by storing them in a nitrogen or argon environment rather than in open air.
3. By applying local laser irradiation annealing method with not more than 0.125 J/cm² increment per pulse, all-silica mirrors are able to withstand superior laser fluences up to 180 J/cm² using nanosecond pulse regime at 355 nm wavelength.
4. Deposition of nanostructured SiO₂ between YAG crystal and dense multilayer coating allows to extend the angular range of TIR in YAG crystals down to 46 deg due to lower effective refractive index.

Approbation

*Scientific papers **directly related** to the thesis (peer-reviewed and indexed in Clarivative Analytics WoS):*

- [A1] **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Near fundamental nanosecond laser damage resistance of nanostructured all-silica mirrors at 355 nm by local laser irradiation”, Results in Optics, 14, 100616, 2024
- [A2] **L. Ramalis**, S. Melnikas, D. Buinovskis, T. Tolenis “Enhancement of total internal reflection in Nd:YAG crystals by multilayer nanostructured coatings”, Optics and Laser Technology, 2025

*Scientific papers **directly related** to the thesis (conferences proceedings):*

- [C1] **L. Ramalis**, L. Grinevičiūtė, R. Buzelis, T. Tolenis “Formation of all-silica sculptured thin films based optical elements on crystal substrates”, Proc. SPIE 11467, Nanoengineering: Fabrication, Properties, Optics, Thin Films, and Devices XVII, 114671V, <https://doi.org/10.1117/12.2568598>, 2020
- [C2] **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”,

Proc. SPIE 11872, Advances in Optical Thin Films VII, 1187210
2021

- [C3] **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, Proc. SPIE 11910, Laser-Induced Damage in Optical Materials, 1191016, <https://doi.org/10.1117/12.2598667>, 2021
- [C4] **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, Proc. SPIE 12202, Nanoengineering: Fabrication, Properties, Optics, Thin Films, and Devices XIX, 1220206, <https://doi.org/10.1117/12.2633935>, 2022
- [C5] **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, Proc. SPIE 12300, Laser-Induced Damage in Optical Materials 2022, 123000O, <https://doi.org/10.1117/12.2641172>, 2022

Other scientific papers (peer-reviewed and indexed in Clarivate Analytics WoS):

- [A3] L. Grinevičiūtė, **L. Ramalis**, R. Buzelis, T. Tolenis “Highly resistant all-silica polarizing coatings for normal incidence applications”, Optics letters, Vol. 46, No. 4, 2021
- [A4] S. Melnikas, **L. Ramalis**, S. Kičas, T. Tolenis “Broadband chirped mirrors with a porous top layer for smooth group delay dispersion”, Appl. Opt. 60, 8181-8187, 2021

Conferences directly related to the thesis:

1. **L. Ramalis**, L. Grinevičiūtė, R. Buzelis, T. Tolenis “Formation of all-silica sculptured thin films based optical elements on crystal substrates”, SPIE. Nanoscience + Engineering, 24-28 August 2020, Oral-Online pr.
2. **L. Ramalis**, L. Grinevičiūtė, R. Buzelis, T. Tolenis “Anisotropic Thin Films Based Polarizing Coatings For High Power Lasers”, Advanced materials and technologies 2020, Palanga, Lithuania, 24-28 August 2020, poster pr.
3. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, Surfaces, Interfaces and Coatings Technologies International conference, Paris, France, 07-09 April 2011, Oral-Online pr.
4. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”,

- SPIE. Optical Design Systems, Digital Forum, 13-17 September 2021, Oral pr.
5. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Skulptūrinių plonų sluoksnių pagrindu suformuoti silicio oksido veidrodžiai didelės galios lazeriams”, Lietuvos Nacionalinė Fizikų Konferencija. Vilnius, Lithuania, 6-8 October 2021, poster pr.
 6. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, SPIE. Laser Damage, 12-15 October 2021, Oral-Online pr.
 7. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, SPIE Nanoscience + Engineering, San Diego, US, 21-26 August 2022, Oral pr.
 8. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, Optical Interference Coatings, Whistler, Canada, 17 June 2022, poster pr.
 9. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, SPIE Laser Damage, Rochester, US, 18-22 September 2022, poster pr.
 10. **L. Ramalis**, A. Strazdas, T. Tolenis “Broad band mirrors using nanostructured thin films”, SPIE. Optical Design Systems, April 7-11 2024, poster pr.

Contribution of the author and others

The contribution of the thesis author and main co-authors are described in the following text:

The author personally designed or actively participated in designing all experiments. The author also performed or supervised all experimental thin film depositional processes, performed spectrophotometric and laser-induced damage threshold measurements. All analysis of nanostructured layers were made by author.

Dr. T. Tolenis supervised the deposition processes, participated in designing of all experiments.

Dr. R. Buzelis participated in all LIDT measurements.

Dr. G. Abromavičius etched fused silica substrates which were used for all single layer depositions.

Dr. A. Selskis performed SEM measurements.

Dr. S. Melnikas performed IBS deposition processes, participated in designing and characterizing of TIR coatings.

Mr. Sebastian Paschel performed LIDT measurements in Laser Zentrum Hannover using different environments

All coauthors participated in preparation of scientific publications.

1. THE LITERATURE OVERVIEW

1.1. Optical elements

Optical coatings play an important role in the world of optics, providing necessary functions to laser systems. Manipulation of the beam path using reflectors, maximizing transmission and reducing undesired reflections would be impossible without optical coatings. With the rapid development of high-power laser systems, optical components remain the weakest points. In order to further develop laser systems, the low stability and limited damage tolerance of optical components need to be improved [11] [12] [13]. Increasing beam diameter dimensions may compensate for the lower resistivity to laser radiation. However, the laser system size will also need to increase. Any improvement in optical elements can have a significant impact on output power or in reducing the size of a laser system. In the past decade, laser systems have advanced significantly, and therefore, there are increasing demands for optical elements, including HR mirrors, antireflective (AR) coatings and total internal reflection (TIR) coatings, particularly in terms of their resistance to laser radiation. In this chapter, the mentioned optical elements will be covered in more detail, as well as some existing improvements.

1.1.1. Anti-reflection coatings

Reflection is an optical phenomenon that occurs when light travels from one medium to another, resulting in a change in the direction of wavefront. All transparent media are characterized by their refractive index, which is the ratio of the speed of light in a vacuum to its speed in the medium. When two media have different refractive indices, light traveling through the interface experiences optical interruption. As a result, a small portion of the light is reflected, this phenomenon is called Fresnel reflection. The incident light which travelled to another medium is termed as transmittance, while bounced back is called reflectance (R). The difference between refractive indices of two mediums is responsible for determining the portion of reflected light.

AR coatings are based on the principle of destructive interference, where reflected waves from different optical interfaces largely cancel each other (see Figure 1). Essentially, AR coatings are designed to create a relative phase shift of 180° between reflected beams from the upper and lower boundaries of a thin film. To achieve this, the optical thickness of the coating must be an odd integer multiple of the quarter wavelength optical thickness (QWOT), which

is optimized to produce a path difference of $\lambda/2$ (phase difference) between R_1 and R_2 as shown in Figure 1 [14].

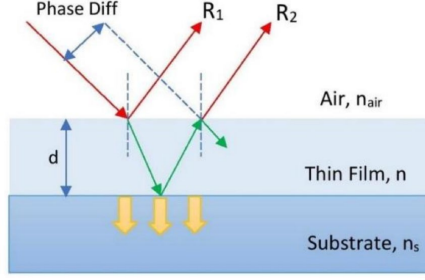


Figure 1. Schematic illustration of light reflected from a single layer [15]

The reflection of the single layer coating can be evaluated using an equation:

$$R = \left(\frac{n_{air}n_s - n^2}{n_{air}n_s + n^2} \right)^2, \quad (1)$$

where R is the reflection, n_{air} is refractive index of air, n_s is refractive index of substrate and n is refractive index of thin film.

Essentially, AR coating must be made from a specific material with a refractive index (n_f) to achieve complete cancellation of the reflected beams. The required refractive index can be determined from equation:

$$n_f = \sqrt{(n_{air} n_s)}. \quad (2)$$

While single-layer AR coatings are widely used, they have certain limitations that makes it difficult to eliminate Fresnel reflections in some cases. It is not always possible to find coating material with the desired refractive index, especially when the substrate medium has a relatively low refractive index. Stacking multiple layers to enhance optical transmittance across a broader wavelength range is also possible using a similar principle. In mathematical models, the vector analysis of individual reflected rays must be considered. The reflection from two layers, i and j , at the interface can be calculated using the following equation:

$$R_{ij} = \frac{n_i \cos \theta_j - n_j \cos \theta_i}{n_i \cos \theta_j + n_j \cos \theta_i}, \quad (3)$$

where R_{ij} is the reflection coefficient, n_i and n_j are the refractive indices of the layers, and θ_i and θ_j are the angles of refraction of incident light, respectively. The total reflection is calculated by summing reflectance from

all layer. This process reduces the total reflection to a minimum value by optimizing the refractive indices and optical film thickness for each layer [16].

1.1.2. Bragg mirrors

In the previous sub-section, we mentioned how destructive interference can reduce Fresnel reflections for the light passing through different media. To increase the reflection, constructive interference is used by forming QWOT ($\lambda/4$) based Bragg mirrors. A multilayer structure of alternating high- and low-refractive-index materials is deposited on a substrate, starting and ending with a high-refractive-index layer material (see Figure 2). To achieve the maximum reflectance for the mirror, we use equation:

$$R_{max} = \left(\frac{n_H^{l+1} - n_L^{l-1} n_3}{n_H^{l+1} + n_L^{l-1} n_3} \right)^2, \quad (4)$$

where n_H and n_L are high and low refractive indices respectively, n_3 is the refractive index of substrate, l is the odd number stack of $\lambda/4$ films. Bragg mirrors are particularly useful in laser systems where high reflectivity is essential for ensuring efficient beam manipulation.

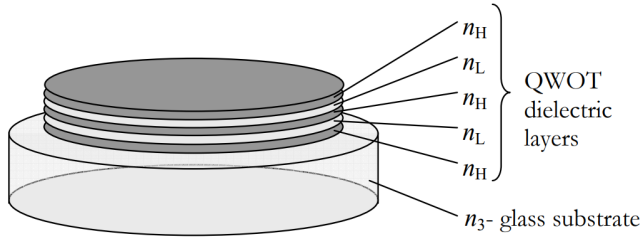


Figure 2. High reflectivity, multilayer dielectric mirror – a stack of low (n_L) and high (n_H) refractive indices layers QWOT[17]

1.1.3. Total internal reflection coatings

Total internal reflection (TIR) effect occurs at the interface between two media with different refractive indices. According to Snell's law, if the angle of incidence reaches the critical angle θ_c and the refractive index of the first medium is larger than the second medium ($n_1 > n_2$), the light beam traveling from the first medium will hit the surface of the second medium and be fully reflected [18]. The critical angle can be calculated using the equation:

$$\theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right), \quad (5)$$

where θ_c is the critical angle, n_1 and n_2 are refractive indices of the first and second media, respectively.

Although, TIR effect fully reflects incident beam, it penetrates a short distance into the second medium at the boundary surface. This interaction creates an evanescent wave, which is on the same order of magnitude as the wavelength. Typically, TIR effect is employed in optical fiber waveguides [19], where the critical angle of incidence is modified chemically to improve performance.

In regard of optical interference coatings, TIR effect is employed in several specific coatings. Such coatings are dedicated to particular applications. For example, combined interference-TIR coatings are used for high AOI beam splitters [20]. Another application of TIR effect include high reflectance coatings for high power slab laser systems [21]. To mitigate thermally induced lensing and birefringence, a zigzag slab architecture is utilized by depositing a low-index coating on the surface of the laser crystal [22]. The coating is actively cooled by connecting it to a heat sink (see Figure 3). The absorption of the coating must be minimized, as strong thermal effects can arise from the electric-field intensity at the crystal surface, adversely affecting beam quality.

Silica is currently the most suitable material for such applications due to its low refractive index and high LIDT. However refractive index of approximately 1.5 achieves a critical angle of around 55° . Various approaches have been developed to decrease the critical angle while maintaining LIDT values [22], [23], [24].

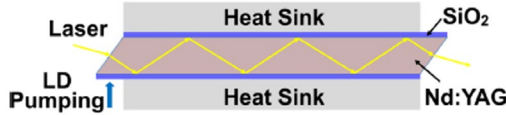


Figure 3. Diagram of zigzag slab laser [22]

1.1.4. Optical coatings on laser crystals

Fresnel reflections occur in every optical component. It is necessary to eliminate them to avoid optical losses. In laser systems, there is a variety of crystals used as a lasing media, such as neodymium-doped yttrium aluminum garnet (Nd:YAG), or for higher harmonic generation, such as lithium triborate (LBO), among others. As laser systems continue to improve, crystals face increasing challenges, and the need to add additional optical functions, such as polarization, wavelength filtering or AR coatings, has become significant. Furthermore, as the laser energies increase, LIDT becomes a critical concern.

Multilayer coatings used to achieve the required optical performance introduce an additional limiting factor, as they can reduce LIDT, lifetime, output power, and the reliability of the laser crystal.

1.1.4.1. AR coatings on LBO crystal

LBO is an excellent nonlinear crystal with high transmission over a wide range (from 160 to 3500 nm) [25]. Moreover, this crystal is notable for its high LIDT and large acceptance angle. It also has strong mechanical properties, such as good hardness and chemical stability, making it a good candidate for high-power density laser beams [26], [27]. As previously mentioned, AR coatings are essential to minimize optical losses. In this application, dual wavelength (frequency) AR coating can be applied. LBO is an anisotropic crystal with distinct optical and thermal properties depending on the direction, and it is partially soluble. These characteristics introduce additional challenges when it is being coated, as they have lower adhesion. Additional interlayer on LBO substrate greatly improves adhesion. However, this interlayer must have a carefully controlled thickness to minimize the impact on the optical performance of the crystal [28].

Recent publications report the use of silica interlayer for frequency doubling coatings (see Figure 4) [29]. SiO_2 layers have demonstrated strong optical performance and improved adhesion on LBO crystals. Interlayers were tested using four different multilayer stack designs and annealing procedures.

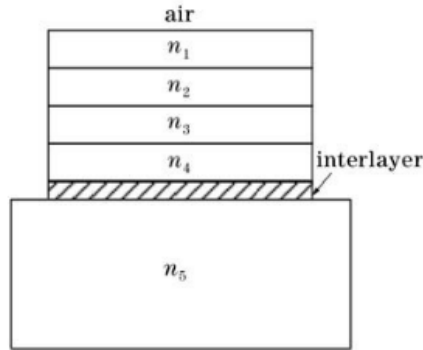


Figure 4. Schematic diagram of a four-layer frequency doubling AR coating with interlayer between coatings and substrate [30]

The highest reflectance was observed without any interlayer. However, during annealing of the optical elements at temperatures up to 473 K after deposition, all coatings survived except for those without a silica interlayer (see Figure 5). This indicates the necessity of an interlayer to enhance adhesion between the AR coating and the LBO crystal surface, despite a slight

decrease in optical performance. In Figure 5 optical micrographs are shown with different AR coating designs.

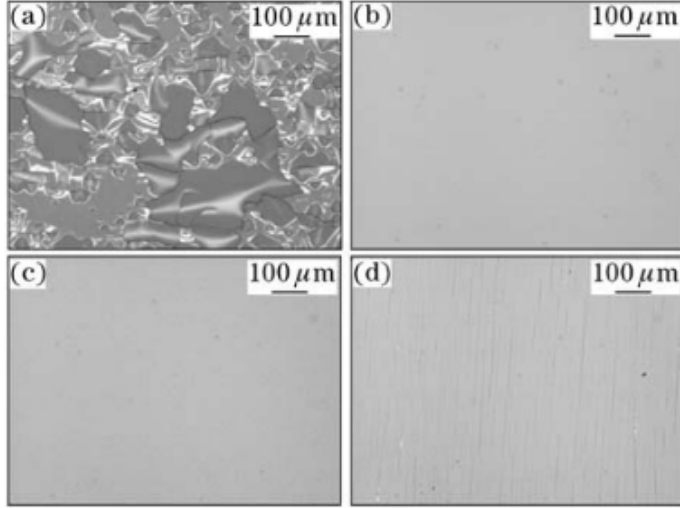


Figure 5. Optical micrographs of the prepared frequency doubling AR coatings with different thicknesses of SiO₂ interlayer [30]. a) without any interlayer, b) 0.1 $\lambda/4$ SiO₂ interlayer, c) 0.3 $\lambda/4$ SiO₂ interlayer and d) 0.5 $\lambda/4$ SiO₂ interlayer

To mitigate adhesion issues, various oxide material mixtures can be used to achieve complex thin-film designs with desired optical properties [31]. Zone target, made of two different metal plates combined together for co-sputtering processes are useful for this purpose. During the deposition process, when an ion beam is directed at the intersection of the two metal plates, a mixture is formed on the substrate. By adjusting the position of the zone target relative to the ion beam, the proportions of different materials can be controlled.

Giedrius Abromavičius compared LIDT values between two AR coatings on LBO crystal using mixed materials. One coating was based on 20-30 % ZrO₂ - SiO₂ mixture, while the other was composed of alternating Al₂O₃/SiO₂ layers [32]. Mixing materials can introduce advantages. For example, ZrO₂ has increased absorption losses at a 355 nm wavelength, as it is close to its resonance absorption edge. By mixing it with SiO₂, this edge shifts toward the UV range, reducing absorption losses. This effect occurs because the band gap changes with the addition of SiO₂ [33]. Al₂O₃ has low UV absorbance, making it a highly suitable material for coatings in the ultraviolet range.

LIDT measurement revealed that the ZrO_2 -based mixture exhibited higher values. The main reason in this case was attributed to the technological factors - alumina stoichiometry may have been incomplete after deposition, leading to microstructure inhomogeneity. Normally, optical components facing these issues are annealed to increase LIDT value. However, LBO crystals are highly sensitive to high temperatures, making it challenging to improve alumina-based AR coating.

There are reports of using the sol-gel method to deposit AR coatings on LBO crystals [13]. This method is preferred for AR coatings in high-peak power laser systems, as it offers high-LIDT coatings, allows controllable refractive indices, and deposition on substrates of various shapes [34]. However, LBO is an anisotropic crystal, which introduces additional challenges in depositing stress-free films. For single-layer AR coatings, no significant issues have been reported. However, after double-layer AR coatings are deposited, the surface often cracks or peels off from the substrate.

Stress measurement was conducted to investigate the effect of sol-gel coating drying time, but no clear correlations were found, as stress levels varied significantly. Although adhesion issues between LBO crystals and coating can negatively affect the lifetime of such crystals, LIDT tests have shown promising results. For example, LIDT values reached 15 J/cm^2 for a 532 nm wavelength with 3 ns pulsed lasers [13].

In order to use laser crystals for second- or third-harmonic generation, besides Fresnel reflections, harmonics separation must be achieved. Detlev Ristau's group conducted research on similar experiments, using more complex coating designs for third harmonic generation on LBO crystals [35]. In their work, AR multilayer coatings were deposited on laser crystals to address multiple wavelengths, and additional dichroic mirrors were added to the laser system to extract a specific harmonic by reflection (see Figure 6).

As mentioned, the main challenges in coating depositions on nonlinear crystals are achieving good adhesion and high LIDT. It becomes even more difficult to fabricate optical elements when coating designs become more complex. In this case, Fresnel reflections had to be reduced for all three harmonics (355 nm, 532 nm and 1064 nm) using AR coatings. One end of the nonlinear crystal was covered with AR coating for two wavelengths (C1 side) while the other side was coated for all three wavelengths (C2 side). Results showed that LIDT values of an uncoated LBO crystal reached approximately 40 J/cm^2 , whereas AR-coated C1 reached 5 J/cm^2 , and C2 reached only 3 J/cm^2 under 355 nm wavelength conditions.

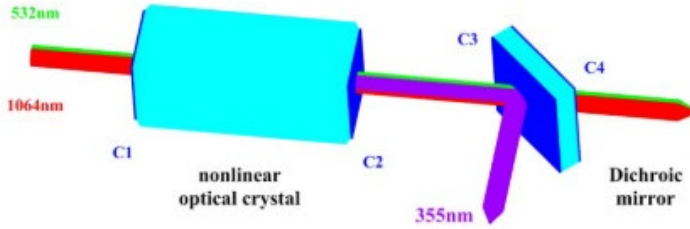


Figure 6. Setup for the generation of third harmonic radiation [35]

This experiment demonstrated that the uncoated LBO crystal had a much longer lifetime compared to the AR-coated crystal when exposed to infrared, green and UV laser radiations. As the coating design becomes more complex, the resistivity of optical element decreases, thereby reducing the output energy of such laser systems.

1.1.4.2. AR coatings on Nd:YAG crystal

Nd:YAG based crystals are less complex compared to LBO crystals and are widely used in solid-state lasers as a lasing medium. Although there are no significant issues regarding coating adhesion or stress induced by anisotropic thermal expansion, coatings remain a limiting factor for these optical elements. Additionally, surface preparation and polishing have a high impact on the LIDT value of the crystal.

There are reports of AR microstructure built into the crystal surface to increase the LIDT of Nd:YAG crystals and eliminate Fresnel reflections [36]. In one study, microstructures were fabricated on the surface of Nd:YAG crystals using two-stage lithography and etching processes. These structures functioned as AR coatings, reducing reflectance for a 1064 nm wavelength to 0.3 %. The LIDT values of the crystal reached up to 21 J/cm², compared to untreated Nd:YAG crystals, which reached only 7.3 J/cm².

This approach represents an alternative to thin-film AR coating technologies. However, deposition techniques that involve applying low resistivity materials onto optical elements and later etching or cleaning the surface show lower LIDT values than traditional coating technologies. It is particularly challenging to clean residual material from the surface after microstructure fabrication, as the remaining material are defects and absorb laser radiation during exposure.

1.2. Resistivity to laser radiation of dielectric coatings

One of the most important characteristics of optical elements is their LIDT, especially in high-intensity laser applications. LIDT is defined as the critical energy density of electromagnetic radiation that an optical element can withstand without any damage. The metrology of LIDT was standardized globally when the International Standards Organization for Standardization has published International Standards (ISO11254-1 and ISO-11254-2) [37], [38]. These standards allow optical components to be based on their resistivity to laser radiation fluence and/or power.

1.2.1. LIDT mechanisms

Every laser pulse carries a certain amount of energy, which is defined by the electromagnetic field of the wave. When a material is exposed to laser radiation, a portion of the energy is transferred to the material's electronic system, causing various physical effects depending on the pulse duration (see Figure 7). For long laser pulse durations (~ 10 ps or longer) linear absorption is the dominant effect, generating free electrons. In other words, electron-phonon interactions occur and laser radiation heats the material due to absorption. The extent of heating depends on the pulse duration, absorption coefficient and reflection properties of the coating.

The absorption of optical elements also depends on substrate and thin film quality, especially the presence of defects. Any impurities before or after the deposition can absorb laser energy, particularly in longer pulse durations (e.g., nanoseconds). Once a defect absorbs laser radiation, it becomes a heating point within the material, leading to a local stress, melting, delamination or cracking of the coating.

Defects are typically particles embedded in the material (nodules), nanometer-sized metal clusters or structural imperfections, such as vacancies that introduce additional energy levels into the bandgap [39], [40]. There defects can originate from molten particulate ejection, solid source particle ejection or flaking of the coating from mechanical parts in the chamber. Such defects significantly reduce the LIDT of the deposited element due to direct laser energy absorption or increased electric-field intensity within the layer structure [41][42].

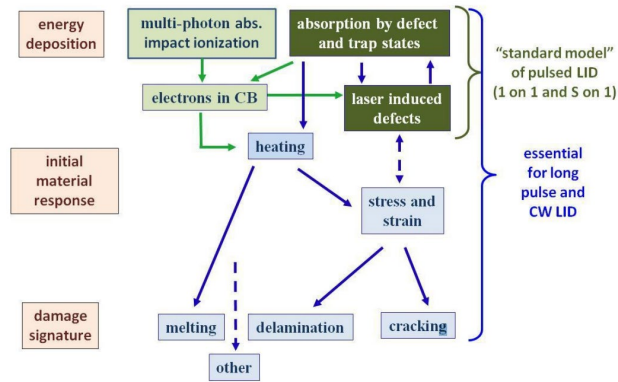


Figure 7. Processes involved in laser damage of optical materials[43]

When the pulse duration is shorter than ~ 10 ps, nonlinear processes become dominant. LIDT becomes dependent on phenomena such as multiphoton absorption, tunneling or linear absorption directly in the band gap, which occur via interband transitions or structural defect states. Electrons are excited and accelerated in the conduction band, transferring their energy to the lattice as heat.

Subsequently, an electron avalanche occurs due to inverse absorption and collisions, leading to an increase in free electron density [44]. This triggers additional physical effects, including photoelectron emission, surface charging and thermalization. Energy of laser pulse is transferred to material lattice by electron-phonon coupling and induces heating of exposed sites [45]. As the temperature increases, melting and high-pressure wave generation occurs, [46] followed by thermal diffusion and lensing effects in the exposed regions [47]. These complex processes drastically influence LIDT values.

1.2.2. Main methods to increase LIDT of optical coatings

In high power laser systems, optical coatings are often the weakest link, limiting the system's total output power. Over years of research laser-material interactions, several methods have been developed to improve the LIDT of optical coatings. In this subsection, key approaches will be reviewed.

1.2.2.1. Layer band gap modification

As mentioned earlier, the band gap energy is a critical material property, that can determine the total LIDT of an optical element (see Figure 8). To ensure optical elements can withstand high intensity laser pulses, high bandgap materials must be selected that also meet the required spectral characteristics. In order to achieve interference effects in multilayer coatings,

at least two: high (H) and low (L) refractive index materials, are needed. In such case high refractive index materials exhibit lower resistance to laser radiation. One approach to improve LIDT is to mix H materials with L ones to form composite materials with higher bandgap energy [48]. However, this also reduces the overall refractive index contrast, which can impact optical performance.

Another method to increase LIDT involves using porous coatings or depositing nanostructured multilayer coatings on top of existing coatings [10]. For example, all-silica multilayer stacks have been used to enhance the LIDT without compromising optical performance. In such designs, the electric field intensity of the laser radiation is reduced within the coating, with maxima occurring in the top layers where high bandgap silica is deposited.

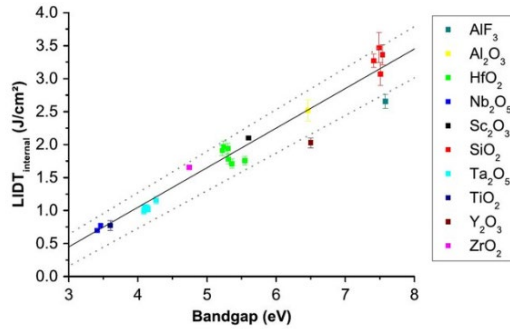


Figure 8. LIDT of coating materials dependency on band gap [7]

1.2.2.2. Post-processing technologies

Additional techniques, such as laser conditioning or annealing, can be employed to increase the LIDT of optical elements [49], [50], [51], [52]. During this process, the optical coating is exposed to laser radiation of a specific pulse duration or a continuous wave, leading to improvements in resistivity.

There are two mechanisms generally considered in laser conditioning process. The first mechanism in this process, laser cleaning, involves removing volatile contaminations, including environmental water, from the surface or bulk of the material. These impurities can cause optical breakdown during LIDT testing. Cleaning contaminants from the bulk material provides a permanent improvement, but surface cleaning is reversible [53][54].

The second mechanism involves laser heating of the material, which induces changes in crystallinity or removes polishing damage. This effect depends on the wavelength of the conditioning laser and the material being treated and is generally considered irreversible [49].

1.3. Thin film deposition methods

Optical coatings can be deposited using a variety of different techniques including purely physical or chemical processes. The most common method would be under vacuum and are classified as PVD techniques. PVD technology is known for producing high-quality coatings with excellent optical and mechanical properties [55]. During the deposition process, thin film growth occurs through condensation of vaporized material directly onto a substrate.

Slightly different methodology is considered chemical vapor deposition (CVD), which uses chemical reactions between precursor materials to form thin films. Both PVD and CVD offer unique advantages, making them valuable in laser optics fabrication. This work focuses on PVD methods for producing dielectric layers.

The most common PVD methods considered to be electron beam deposition (EBD) and sputtering. In EBD the material is being heated locally by electrons to the temperature at which it vaporizes and vapor then condenses on the substrate. Using sputtering method, the vapor is produced by bombarding the target with energetic particles, making the molecules or atoms eject from source material [56].

1.3.1. EBD method

The most common PVD method used for optical coating production is thermal evaporation. Figure 9 illustrates the principle of this process. Several techniques are used for evaporation, including resistive heating, EBD and plasma assisted EBD.

The simplest approach is resistive heating. It involves placing the material to be evaporated in a resistively heated crucible. The material may be attached to a heating wire or strip. The crucible is heated until the material reaches high enough temperature to evaporate. For larger volumes, a crucible is often used, typically in the form of a resistive boat. However, this method has limitations, as the material's evaporation or sublimation temperature must be lower than the boat's material.

EBD overcomes this limitation melting material locally with a focused electron beam, while the crucible is actively cooled. This enables the evaporation of a wider range of materials. Additionally, EBD offers better control of growth rate, reduces defects and conserves material.

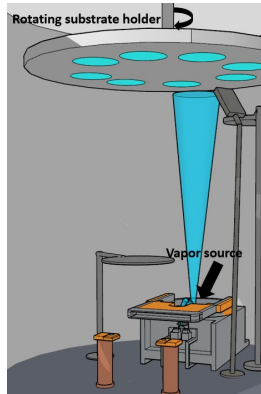


Figure 9. Principle schematic of the basic features of EBD

Despite its simplicity, achieving high-quality coatings via PVD requires careful consideration of various parameters. The vacuum level in the chamber is critical, as it determines the remaining energy of evaporated atoms and the degree of background pressure. The cleanliness of the chamber also affects coating quality. Other important factors include evaporation rate, substrate material, substrate temperature, etc. which has a high influence for the final coating quality as well [57].

During this work, plasma assisted EBD from Altechna will be used to deposit standard multilayer coating of 15 dense $\text{HfO}_2/\text{SiO}_2$ on top of GLAD coating. Depositions were done by using additional heating of 80 degrees and oxygen flow to obtain fully oxidized coatings. In order to obtain high quality hafnia/silica coatings, annealing of the coatings is necessary [58]. In this case, the microstructure of these layer can be formed with different polycrystalline structure, which may affect LIDT value or other optical characteristics of the coating. However, to avoid additional heating of the coating after deposition process, plasma assisted process is used.

1.3.2. Ion beam sputtering method

Another widely used technique for producing thin films is ion beam sputtering method, a PVD method based on ballistic processes. In this technique, energetic particles (ions) are generated in separate ion source and directed to material target. Collision with a target material results in transferring energy and momentum to the target's atoms [59]. During this interaction, several processes occur, including sputtering, scattering and implantation (see Figure 10). When primary ions collide with target material with sufficient energy to break chemical bonds, target atoms are ejected from the surface to form a vapor flux.

Similar to the thermal evaporation, this vapor flux travels through vacuum chamber and condenses onto the substrate. However, in IBS, the sputtered particles have higher energy, producing layers with bulk-like density [31]. These films exhibit excellent optical and mechanical properties, with low absorption and scattering losses.

One drawback of IBS is the internal stress in deposited layers, which can induce optical element breakdown during laser radiation exposure [60].

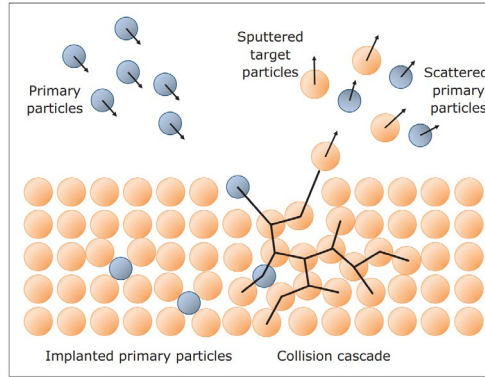


Figure 10. Sketch of selected fundamental processes that occur due to ion-solid interaction [59]

During this work, standard IBS coating of 11 dense $\text{Ta}_2\text{O}_5/\text{SiO}_2$ will be deposited on top of GLAD coating. By sputtering Ta and Si metal targets, deposition pressure was maintained at 2×10^{-4} mbar using oxygen flow of 40 sccm (standard cubic centimeters per minute) and 80 sccm, respectively. To ensure precision of 1 %, broad band optical monitoring system was used for thickness controll.

1.3.3. Evolution of thin films

The deposition process of thin films is characterized by three stages: nucleation, condensation and layer formation. During nucleation, atoms or molecules, evaporated from the source impinge on the substrate. At this point, particles may either adhere to the surface or reflect away. If a particle is physically absorbed, it becomes an adatom and may diffuse over the substrate. Depending on its energy the adatom may be desorbed (re-evaporated from surface) or it is adhered to a location where its energy is at a local minimum [61].

The ratio of absorbed atoms to the total number of impinging particles is defined as the sticking coefficient [3]. The mobility of adatom depends on their energy, the chemical bonds between the atoms and the surface and the substrate temperature. As more adatoms accumulate, re-evaporation becomes less likely and clusters begin to form. These clusters eventually grow into nuclei, which randomly distribute across the surface.

However, when energetic minima are present in the substrate, they may influence the distribution of nucleation centers. Such energetic minima can form due to crystalline structure of the substrate, surface roughness, film material, flux and kinetic energy of particles, growth temperature, or oblique-incidence deposition [62]. In typical EBD evaporation method, kinetic energy of incident flux reaches around 100 meV and in ion beam sputtering processes, the ejected atoms energies may reach up to 10 eV. These energies are also dependent on fabrication parameters, including vacuum level, deposition rate, temperature, etc. Thin film growth – nucleation formation of evaporated atoms describes optical properties of deposited layers, however theoretical models do not completely agree with experimental results considering homogeneous distribution of layers properties. Various theoretical models describing thin film growth must be considered to identify internal structure or optical parameters of the coating.

In the middle of the twentieth century the deposition of thin films was divided into three major models, depending on the energy in the interface between the film and the substrate. *Frank and van der Merwe* model describes layer-by-layer growth (continuous layer), when the interaction energy between the substrate and adatoms is greater than atomic bond energy within the film.

$$\gamma_B > \gamma^* + \gamma_A, \quad (6)$$

where γ_B is the substrate surface energy, γ^* is the film surface energy and γ_A is the energy of coating material.

Volmer-Weber model assumes that crystalline films grow as individual islands, forming 3D nuclei when the interfacial energy dominates. In this case individual islands are formed when:

$$\gamma_B < \gamma^* + \gamma_A, \quad (7)$$

Stranski-Kranstanov model is based on atomistic calculations, describing intermediary process characterized by both 2D layer and 3D island growth. Beyond a critical layer thickness of the deposited film, growth continues through the nucleation and coalescence of absorbate islands[63].

As all of these three models were unified, epitaxy and prediction of the growth mode were achieved by Bauer [64]. Basically, as the number of adatoms increase, island growth is initiated. Island formation grows large enough to touch each other and coalescence takes place. At this point surface free energy is minimized.

Further morphology and texture of microstructure of deposited film is described. One of the first models to describe it was published by Movchan and Demchishin [65]. Here model is introduced for evaporated metals and oxides, how morphology is dependent on the ratios of substrate temperature T and melting temperature of the material which is used T_m . Layers were made by EBD evaporation method with the thickness of $300\text{ }\mu\text{m} - 2\text{ mm}$. They used metal (Ti, Ni, W, Fe) materials and oxides (ZrO_2 and Al_2O_3) for the depositions. They separated gained coating structures into three zones (see Figure 11):

- *Zone 1* ($T/T_m < 0.3$) displays a porous structure. High number of dislocations in the inner crystalline materials.
- *Zone 2* ($0.3 < T/T_m < 0.5$) consists of columnar shape crystals. In this zone, surface diffusion takes place with an activation energy of $0.1 - 0.3\text{ eV}$, which decreases the effect of shadowing. The density of the films is larger as well as the distribution of the crystallites and the surface is smoother.
- *Zone 3* ($T/T_m > 0.5$) consists of equiaxed grains. Bulk diffusion is dominant process with an activation energy larger than 0.3 eV . The structure of film corresponds to fully annealed metal.

The model was further extended to include argon sputtering conditions by J. A. Thornton [66], who added pressure dependence of the morphology. The structure of layers is described not only by the temperature of the substrate, but also with pressure of added gas during deposition process. In this case additional intermediate transition (T) between *Zones 1* and *2* appears, which contains similar inner structure as in *Zone 1*. The surface diffusion overcomes the initial nucleation of the substrate. Simply by adding additional argon pressure, the energy changes in particles due to thermalization. When adatoms have no mobility to diffuse into gaps formed by shadowing effect due to low energy, first zone is obtained. This may occur to amorphous and crystalline coatings.

Further improvement of structural zone model was made by R. Messier, who included ion-assistance influence with sputter deposition method [67]. The model was additionally supplemented by C. R. M. Grovenor how substrate morphology affects microstructure of the film [68].

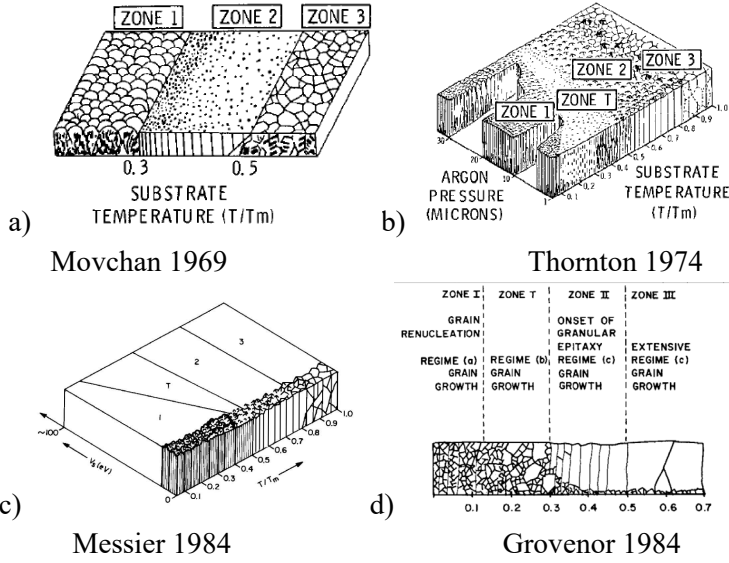
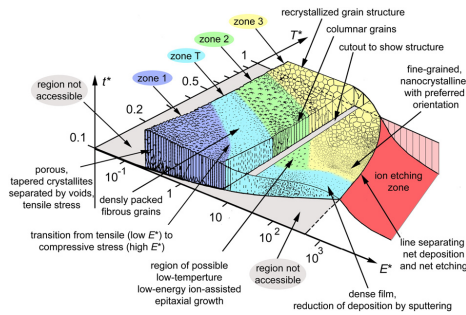


Figure 11. Structural zone models: a) B. A. Movchan, b) J. A. Thornton, c) R. Messier and d) C. R. M. Grovenor [69]

By analyzing thin films structures, deposited by magnetron sputtering method, Anders extended structure zone model by adding the effect of ion etching (see Figure 12) [70]. Proposed structural zone model in this case is more universal and applicable in most cases, when three axes were changed: temperature, normalized kinetic energy and coating thickness. Anders model is applied for deposition methods with high energy flux (greater than the bounding energy of formed thin film). However, the structure of thin films is primarily dependent on initial parameters of deposition method, including vacuum level, deposition rate, etc.



1.3.4. GLAD

Sculptured thin films concept was enunciated in 1996 by A. Lakhtakia group [71], although structural coatings were known for over several decades. In the optical coatings industry, the anisotropic film deposition was recognized before [72], [73], however there were no perfect way to visibly see created nanostructures before the advent of scanning electron microscope (SEM). Optical coatings engineers tried speculating how oblique vapor deposition can influence dielectric polarization properties by explaining anisotropic permittivity occurring from columnar microstructure. Young and Kowal formed sculptured thin films by continuously altering the substrate orientation to create predicted transmission optical activity, this way sculptured thin films were observed without SEM imaging [74]. They were the first group that engineered thin film morphology to produce sculptured thin films.

GLAD is a PVD extension where substrate is tilted during the process to induce nanostructured materials fabricated in a controllable manner (see Figure 13). This includes the ability to instantaneously change the growth direction by using two stepper motor system and form a wide spectrum of columnar forms [75], [76], [77]. During deposition process, the tilt of a substrate is adjusted at a specific angle χ in terms of the vapor flux. Upon having low temperatures and arriving atoms with very low energies, the sticking coefficient is high, thus there is no surface diffusion [78]. As the atoms condense on the substrate, they immediately form a nuclei and ballistic shadowing effect influences the further growth of the layer [79]. As the tilt angle increases, shadowing effect prevents incoming vapor from condensing into regions behind the nuclei and the coating begins to form a more porous columnar structure.

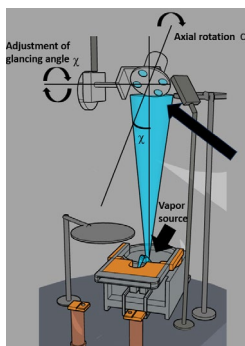


Figure 13. The principal scheme of GLAD

The concept of columnar structure orientation growth due to shadowing effect is not so straightforward. To induce columnar formation, the tilted angle has to be from 30° up to 90° , however, the column's inclination angle (β) is not the same as the evaporation tilt angle (χ) (see Figure 14). The relationship between these angles is published by Nieuwenhuizen and Haanstra [80]. By empirically describing experimental data, they proposed such geometrical relation:

$$\tan \chi = 2 \tan \beta. \quad (8)$$

As the analysis were performed more precise, geometric relationship was improved by Tait[81]. The tilt of columns can be evaluated using relation:

$$\beta = \chi - \arcsin \left(\frac{1 - \cos \chi}{2} \right), \quad (9)$$

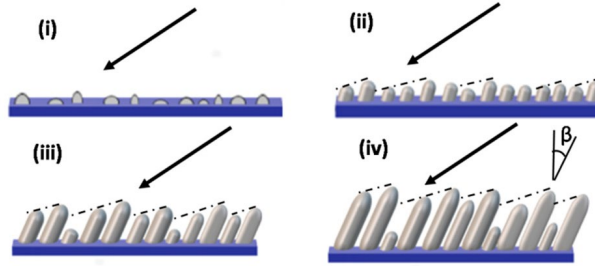


Figure 14. Atom formation on substrate due to shadowing effect: (i) incident vapor flux, shown by full arrows at an angle (χ), resulting in random nucleation. (ii) Nucleus growth casting a nearby shadow, as shown by dotted lines. (iii) Column growth progress, suppressing neighbors' growth via shadowing. (iv) Full column growth at a certain specific angle (β) with respect to the normal [82]

By combining shadowing effect and substrate rotation around its axis (α), the growing film acts as its own shadowing mask, which can be manipulated during the deposition to steer columns into the desired geometry as shown in Figure 15 [79]. Many different GLAD processes have been developed by inducing shadowing effect and controlling two stepper motors system.

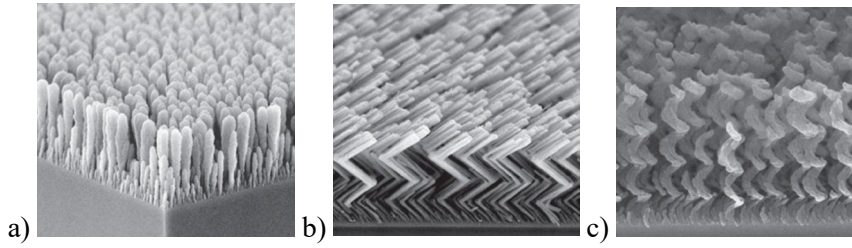


Figure 15. SEM images of nanostructured columnar films: a) vertical, b) zigzag and c) helical columnar morphology [79]

Such nanostructured thin films may be widely used in manufacturing optical elements including AR [9], HR mirror [8] or more complex coatings [83]. The use of nanostructured coatings has a big advantage over conventional techniques as it can form optical element using a single material, such as silica, which is highly resistant to laser radiation due to its large band gap width.

During this work, GLAD method will be used in order to form single-layers for several different materials at different angles as the rotation around substrate axis is kept constant. In this case, vertical columns are initiated, when substrate tilt angle is not 0° . After analyzing single-layer coatings, a multilayer coating will be formed using single material – SiO_2 . Such structure was already demonstrated previously [8], [10], where separate layers are formed by changing the tilt angle of substrate. However, such elements have several issues, regarding environmental degradation. Elements, formed using GLAD method have spectral instabilities as well as LIDT instabilities, which complicates the use of such mirrors in real life laser system.

1.4. Conclusion

GLAD method is used to analyze porous structures, which could potentially be applied for laser systems. By using single material, main optical elements, including AR, HR and TIR, will be formed and their optical characteristics will be analyzed. Spectral stability, LIDT and structural properties measurements will be done in order to understand porous coatings more in depth. Multilayer sculptured thin films will be deposited on YAG laser crystal in order to expand applications of porous layers. TIR effect will be improved by depositing YAG laser crystal with a combination of GLAD coatings and IBS or EBD.

2. ANALYSIS AND EXPERIMENTAL SET-UPS

2.1. Optical measurements

2.1.1. Spectrophotometric measurements

All coatings were measured using Photon RT (EssentOptics, Lithuania) spectrophotometer in order to evaluate spectral performance of coatings including TIR effect. Spectrophotometer can operate from 185 nm to 2600 nm wavelength, with accuracy of ± 1 nm, angle of beam divergence of ± 1 degree. For coatings deposited on FS substrates we used standard configuration (see Figure 16 a)) to measure transmittance and reflectance spectra. For coatings deposited on YAG crystals measurements were carried out after inserting custom holder for polarizing cube measurement and carefully aligning the prism perpendicularly to light beam. During such measurements of YAG prisms we noticed that the light beam converges at small degree before the sample and diverges after the sample. The divergence angle is small enough to be ignored for standard optical coating measurement applications. However, as following modelling indicates, in our case even such a small divergence angle impacts the spectral parameters of the coating.

Also, it should be noted that during measurement light enters the prism from side surfaces at an incident angle close to 0° (see Figure 16 b)). In this case the angle at the coating inside YAG prism is not exactly 45° when the incident angle is not exactly 0° at side surface due to different refractive index of YAG prism. Therefore it is bent accordingly to Snell's law. Therefore, there is a difference in the intended incident angle and internal incident angle at which the light actually enters the coating.

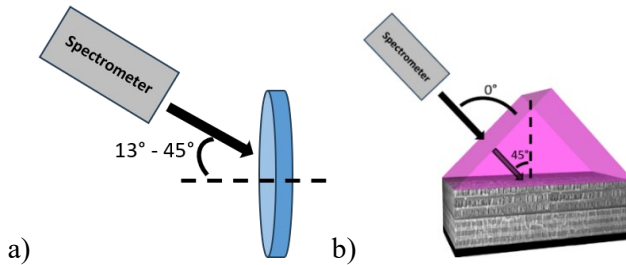


Figure 16. Principal scheme of spectrometer measurement using a) standard configuration and b) TIR configuration

2.1.2. White light interferometry

HeNe laser interferometric microscopy measurements were done using the „Zygo Virefire” equipment. The system is used to provide FS substrates and coatings surface measurements of flatness. 1 mm thickness substrates were used for measurements. One of the criteria for high-quality coatings is stress, which may induce various unwanted effects including failure of coating while interacting with laser radiation. White light interferometry is used to detect curvature changes on FS substrate after it is coated and by applying Stoney formula:

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{h_s^2}{h_f} \left(\frac{1}{R} - \frac{1}{R_0} \right), \quad (10)$$

where E_s is the Young's modulus, ν_s - the Poisson's ratio, h_s - the thickness of the substrate, h_f - the thickness of the film, R and R_0 are the curvature radii of the substrate after and before deposition respectively. The curvature of substrate was calculated using geometrical formula of:

$$R = \frac{L^2}{8h}, \quad (11)$$

where L is the diameter and h is the difference between the peak or valley of the scan and the edge.

2.1.3. Laser-induced deflection

Absorption measurements were performed by laser-induced deflection (LID) device (see Figure 17) developed by *Leibniz institute for photonic technologies* [84]. Measurements were done using 355 nm wavelength, 60 kHz pulsed laser with a beam spot diameter of 1 mm. For 355 nm wavelength, minimum absorption measured can be around 10 ppm with error of +/-5 ppm. The method is based on the measurement of the beam deflection due to thermal lensing caused by absorption on substrate surface. The experimental setup contains excitation and probe laser beams, which are directed to the sample. The excitation beam is absorbed by the substrate surface, causing a thermal lensing effect. The probe beams are therefore deflected due to thermal lensing. The absorption is calculated by comparing probe beam shift with calibrated values. In this method, a pulsed laser with high repetition rate is used to generate the excitation beam.

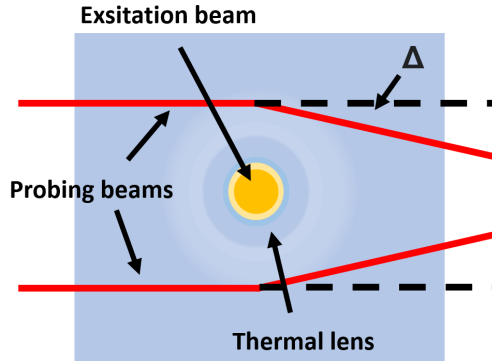


Figure 17. Experimental setup of LID

2.1.4. Laser-induced damage threshold measurements

Two different set-ups were used to perform LIDT measurements. First laser system consist of pulsed Nd:YAG laser (model Ekspla NL 120) (see Figure 18). All LIDT measurements has 5 % absolute errors. Third harmonic (355 nm wavelength) was used for most of the measurements with the repetition rate of 15 Hz and pulse duration of 2.08 ns, with beam diameter – 61 μm . Also second harmonic was used with the same parameters for other LIDT measurements. Nd:YAG lasers are used by many researchers making it one of the most popular device in laser systems. This is the main reason why according wavelength optical elements were formed during disertation. For the first part, standard 1-on-1 method (ISO21254:2011[85]) was used by exposing sample with laser radiation in 12x12 matrix. Different energy fluences ranging from 2 J/cm² to 120 J/cm² were used, afterwards optical microscope inspection is performed for final evaluation of damaged spots.

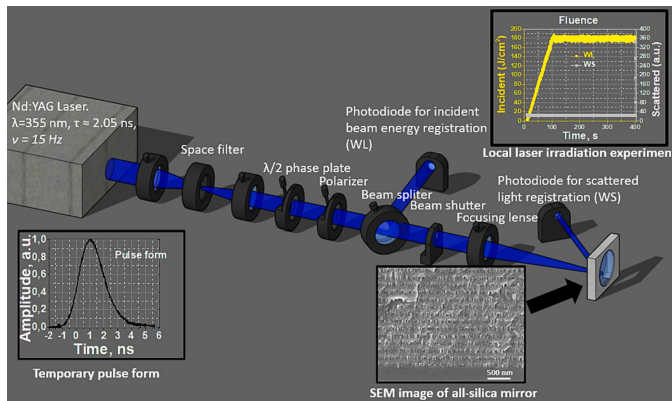


Figure 18. Experimental setup for LIDT 1-on-1 and ramping tests [86]

Afterwards, ramping method was used using the same set-up, where the samples were locally exposed to laser radiation. Exposure starts with the incident fluence of 10 J/cm^2 (selected value is lower than gained value of 1-on-1 tests) and it is increased with specific increment per pulse. Irradiation is stopped when scattered light detector value is increased drastically, meaning that the damage occurred on optical element surface. Elements were measured 10 times in different spots with different increment per pulse for more precise results.

Another set-up was used for LIDT measurements using femtosecond laser pulses. The damage testing of coatings was done using ELI Beamlines 37 fs pulse duration, 805 nm wavelength, 1 kHz repetition rate laser and $120 \mu\text{m}$ beam diameter [87]. All samples were measured under vacuum of approximately 1×10^{-6} mbar.

2.2. Structural measurements

2.2.1. SEM

Images of samples surface and cross-section were produced using SEM (Helios Nanolab 650 (USA)). Coatings were deposited on Si wafer, afterwards, the samples were broken in half and coated with 20 nm Cr layer in case of charging effect. This device offers high precision 5-axes motorized stage with the resolution of 0.9 nm across the whole 1-30 kV range. When a sample is radiated with an electron beam, elastic scattering results from the atomic nucleus or the outer shell electrons with similar energy. After the incident electrons are scattered, they are called backscattered electrons, which are observed by detectors. During inelastic scattering interactions, the accelerated electrons transfer their energy to the atoms of sample, causing other physical effects, including electron excitation, which leads to generation of secondary electrons. These secondary electrons are mostly used for SEM imaging.

2.2.2. Atomic force microscope

Dimension Edge of Bruker Atomic force microscope (AFM) was used to measure samples surface topography. To avoid destruction of porous structures, dynamic contact mode (or tapping mode) was used to investigate surface roughness or damaged spots after LIDT measurement for deeper understanding the origin of damage. In case of tapping mode, the cantilever is driven to oscillate up and down at its resonance frequency. AFM image is

produced by imaging the force of the contact of the tip with the sample surface [88].

2.2.3. Raman scattering spectroscopy

Raman scattering spectroscopy was used to determine molecular changes in samples after exposing them to different environments. Coatings produced in this work are highly porous, thus when exposed to various environments, it may absorb harmful particles, including water, which lowers the resistivity to laser radiation of optical element. CaF_2 substrates were used to reduce various unique optical properties which may affect Raman spectra in distinct ways. FT-Raman spectrometer MultiRAM (Bruker) was used for these experiments. Collected spectra range in the wavenumber region from 4000 cm^{-1} to 150 cm^{-1} .

2.3. Preparation of samples

A great care for substrates surface must be applied to reduce any harmful contamination before deposition process. Each substrate was cleaned in an ultrasonic bath, which is held in the clean room. In case of single layer depositions, substrates were additionally etched with plasma to avoid any stress or cracks of Beilby layer [89].

All porous coatings were deposited using EBD technique with Sidrabe (Latvia) vacuum chamber. In case of SiO_2 material, growth rate was maintained at 3 Å/s , for all other materials it was held at either $1\text{--}2\text{ Å/s}$. Depositions were done at 1.5×10^{-5} mbar pressure and no external heating was applied. GLAD method (see Figure 13) was used for all porous single layers or multilayer structures. During the process, substrate was tilted at specific angle while it was rotated around its axis at approximately 0.5 Hz frequency. Quarts monitoring system was used for precise control of thickness during the process, which was calibrated by adjusting tooling factor of test experiments.

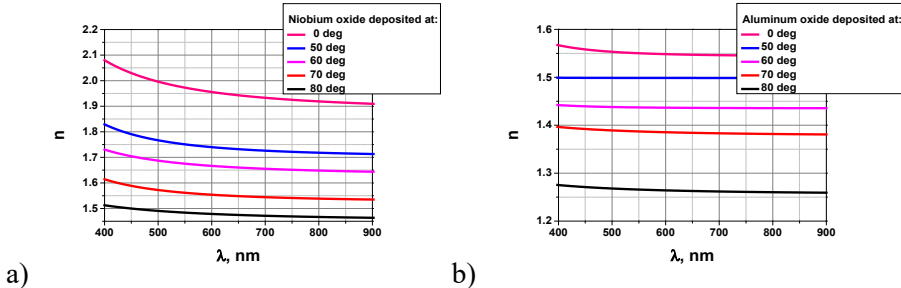
3. RESULTS

A series of experiments was conducted to better understand porous coatings deposited using the GLAD method. Firstly, four different materials (Nb_2O_5 , Al_2O_3 , Ta_2O_5 and SiO_2) were analyzed to investigate LIDT dependency on porosity. Five different angles for single layers of each material were selected χ : 0° , 50° , 60° , 70° and 80° . The thickness for each single layer was 5 QWOT at 532 nm. The electric field through the layers changes as the optical thickness changes, especially for high-refractive-index materials. In order to avoid E-field influence, the optical thickness was kept constant for all layers. Porous coatings tend to absorb water or other harmful particles from the environment, so all samples were stored in a glass desiccator filled with silica gel after the deposition process. The investigation of optical and structural properties was performed. All of the single layers were deposited without any heating during process, however in niobium oxide case, all of the coatings were additionally annealed at 400°C for 1 hour to insure oxidation process.

3.1.1. The analysis of single layer of different materials

Material related to this chapter was published in [C1, C2, C3]

Optical investigations of single layers of different materials deposited at various angles were performed. Spectrometer measurements were done to evaluate refractive indices for each layer using OptiLayer software (see Figure 19). As the deposition angle increases, the shadowing effect increases, making the structure of the coatings more porous and leading to the decrease of refractive index [90], [91]. This effect occurs only in low-energy deposition processes, such as EBD technologies. Similar results are obtained by other researchers, who analysis sculptured thin films [90], [91], [92]. The refractive index due to shadowing effect is being constantly reduced as the tilt angle of substrate increases.



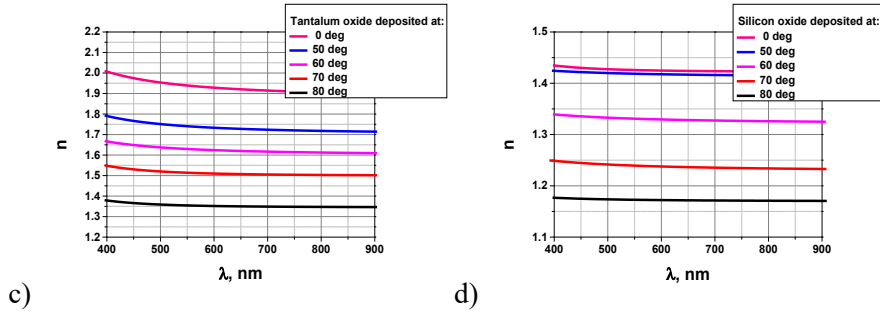


Figure 19. Refractive index dispersions of a) niobium oxide, b) aluminum oxide, c) tantalum oxide and d) silica reported at different angles by GLAD method

The porosity of each single layer can be calculated using Bruggeman Efficient Media Theory (EMT) [93]:

$$p \frac{\varepsilon_A - \varepsilon_e}{\varepsilon_A + 2\varepsilon_e} + (1 - p) \frac{\varepsilon_B - \varepsilon_e}{\varepsilon_B + 2\varepsilon_e} = 0, \quad (12)$$

where p is the porosity (or filling factor), ε_A , ε_B and ε_e are dielectric function of the high refractive-index material, the low refractive-index material and the effective-medium material, respectively.

Generally, effective refractive indices are compared with each material's bulk refractive index to calculate the porosity of each single layer. The porosity of each single layer is presented in Figure 20. A similar tendency was reported in other scientific researches [[90], [91]].

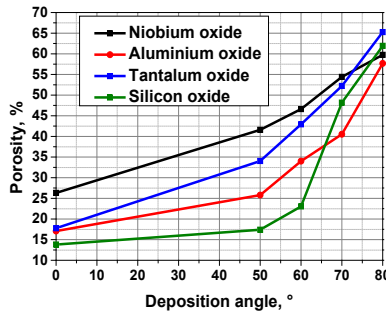


Figure 20. Porosity dependance on deposition angle of single layers for Niobium oxide, aluminum oxide and tantalum oxide

Porosity dependance on deposition angle images (see Figure 20) showed that the structures of all materials grew differently. SEM images were obtained for inner structure inspection of single layer coatings cross-section and top (see Figure 21 and Figure 22). After analyzing SEM images we observed

similar tendencies, starting from niobium oxide coatings, where columnar structure formation occurs from 50° deposition angle. From these results we can see, that niobium oxide is most porous material, however at 80° angle of deposition we can see, that porosity drops compared with other materials. From SEM image we observe the expansion of columns. At the beginning of film growth, columns are ~38 nm wide and at the end the column expands to ~70 nm. This may explain the porosity decrease of layer as this effect is well known in GLAD method. Competitive columnar growth occurs in such coatings causing smaller columns to merge making bigger ones, while the width of the column increases [82].

Upon analyzing SEM images of alumina, we observed a clear formation of columnar growth beginning at a 70° deposition angle. At 80° angle of incidence, we observe the same, non-uniform columnar growth effect, where the width of columns reaches ~23 nm and expand to ~42 nm at the end. After analyzing top view of films, layer formed at 80° differs from other layers – we observe columnar island formation. As mentioned before, before SEM measurement all of the coatings are sputtered with a thin (20 nm) Cr layer to avoid charging effect, however in top view of layer formed at 70°, we observe cracks, which indicate the electron accumulation at the top of columns.

In the case of tantalum and silica layers, we observed relatively similar structural growth. In both cases, columnar structures start forming at deposition angle of 60° and above. Although the cross-section images are similar in terms of the structure, the porosity of tantalum is higher. SEM images of silica layers from top shows less porosity, meaning that competitive columnar growth effect is stronger for these coatings.

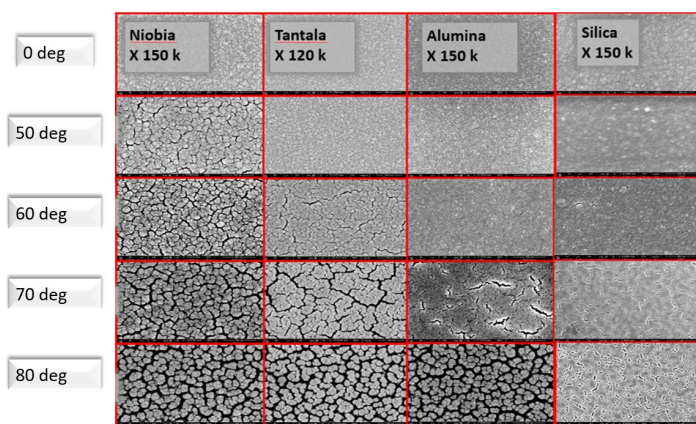


Figure 21. SEM measurements of niobium oxide, aluminum oxide, tantalum oxide and silicon oxide single layers top formed at different deposition angles

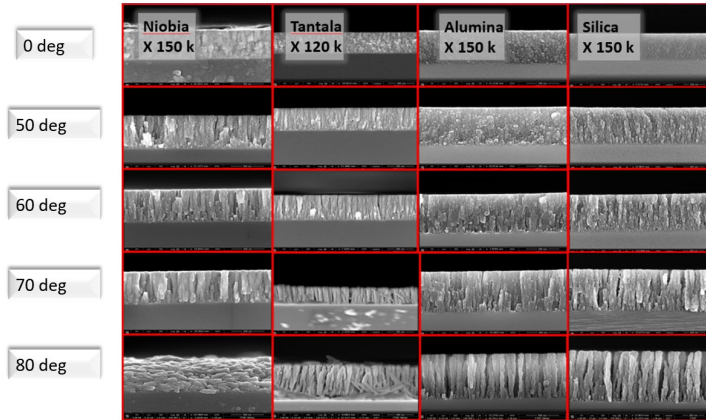


Figure 22. SEM measurements of niobium oxide, aluminum oxide, tantalum oxide and silicon oxide single layers cross-section at different deposition angles

It is worth mentioning, that in order to apply SEM measurements, the silicium plate with coating must be cracked in half and one coating haven't survived this procedure (see Figure 22). Cross-section image of niobia deposited at 80 degrees reveals, that all columns are broken. However from top view of the same coating we can clearly see that the columns are standing up, so probably columns got broken during the silicium plate cracking.

Porosity was additionally evaluated using SEM top-view images and compared with the porosity of each layers calculated using the effective medium approximation method (see Figure 23). Images were analyzed using „ImageJ” software. The increase of porosity with the increase of deposition angle due to shadowing effect occurs in all coatings. This tendency is observed in cross-section and top SEM images. However, there is a clear difference in porosity values while comparing effective medium approximation with SEM top images. Such difference appeared due to competitive columnar growth effect, as the porosity evaluation from SEM images covers only the top of layers. Spectrometer measurements are more accurate, because the films are analyzed as an averaged medium. In both cases, niobium oxide porosity is highest and changes linearly (according to SEM top images), while other materials can be separated into two stages: from $\chi=0^\circ$ to $\chi=60^\circ$ weak growth and from $\chi=60^\circ$ to $\chi=80^\circ$ strong growth of porosity occurs.

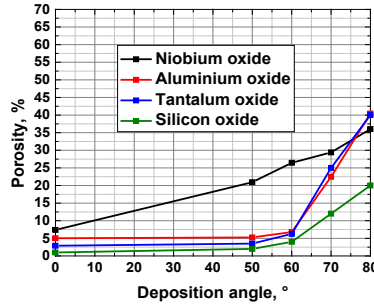


Figure 23. Porosity of niobium oxide, aluminum oxide, tantalum oxide and silicon oxide formed at different deposition angles from SEM measurements

The next step was to investigate the resistance to laser radiation of each single layer coating to determine how porosity affects LIDT for different materials. As mentioned previously, the thickness of all single layers was held at 5 QWOT of 532 nm to prevent any effect of electric field during LIDT measurement. Due to different effective refractive index of each layer, a slight difference of electric field at 532 nm wavelength is still visible, which may have influenced resistance to laser radiation (see Figure 24).

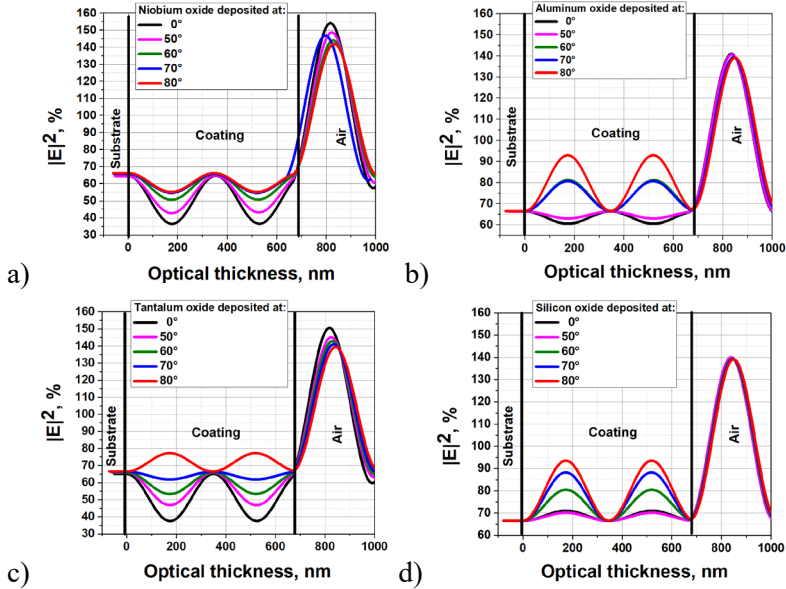


Figure 24 Electric field distribution at 532 nm wavelength throughout a) niobium oxide, b) aluminum oxide, c) tantalum oxide and d) silicon oxide single layer coatings

Laser damage testing measurements were performed in the 1-on-1 mode using 532 nm wavelength, 2.05 ns, 80 μm diameter, 15 Hz pulsed laser setup (see Figure 25). In case of alumina, it is difficult to evaluate results due to the lack of an accurate correlation between resistance to laser radiation and porosity. LIDT value is around 32.29 J/cm² for all coatings with different deposition angles. In case of niobium oxide, thin film formed at 0° angle exhibits the highest resistivity (13 J/cm²). For Ta₂O₅ coatings, the dense layer has the lowest threshold to laser radiation (12.5 J/cm²). In silica case, layers formed at 70° and 80° has lowest LIDT values (~60-70 J/cm²), while other layers reach >100 J/cm².

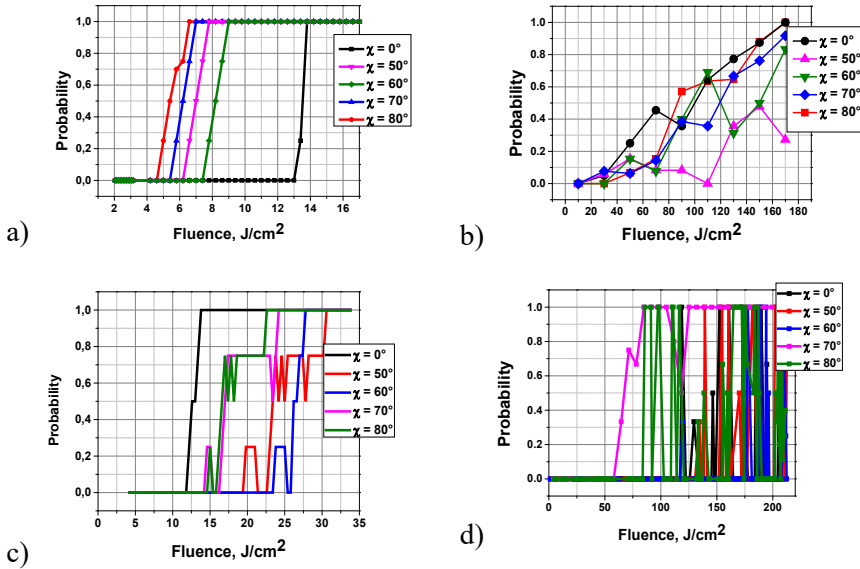


Figure 25. Damage probability for a) niobium oxide, b) aluminum oxide, c) tantalum oxide and d) silicon oxide single layers deposited at different angles

Characterizations of single layers revealed that there is no clear correlation between porosity and resistance to laser radiation for single-layer coatings. Different materials have different dependencies, which are difficult to determine. LIDT exhibits different damage mechanisms depending on pulse length. For lengths up to 10⁻⁸ s damage threshold is most likely to be linked to thermal properties (thermal capacity, heat conduction and melting point) and may induce other damage mechanisms including dielectric breakdown [94]. Thermal damage mechanism is also caused by defects, formed during deposition process or from environment. In Figure 26 we can see how morphologies of all single layer coatings look after LIDT measurements.

Observed morphologies are very similar to defect caused morphologies in coatings [52]. Porous single layers are more likely to absorb various gases from the environment, including hydrogen and other harmful particles, causing the coating to degrade over time. Such defects have a big impact to LIDT results, especially in ns regime [95].

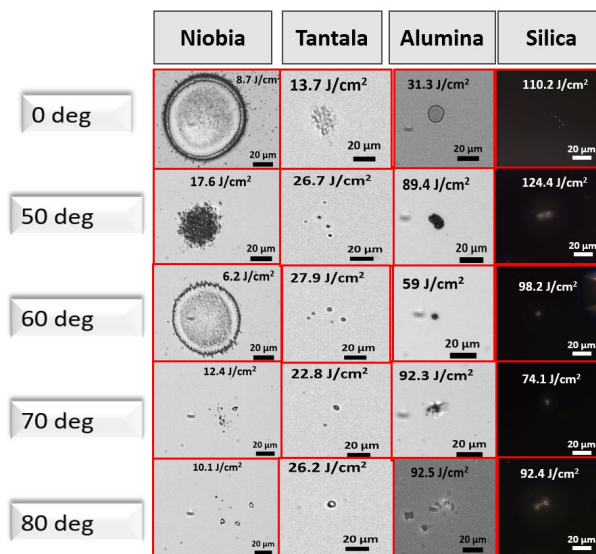


Figure 26 Optical microscope images of all single layers after LIDT measurements

In case of sol-gel monolayer film formation, the porosity plays minor role, which may affect LIDT values [96]. Formation of ZrO_2 and SiO_2 monolayer films with different porosity may result in different optical parameters, such as absorption or LIDT. However in this case, the coating deposition method was different, which could have had an impact on layer formation. In our case, the deposition method remained the same for all single-layer coatings only deposition angle being different.

It is known from the literature, that some materials are more resistive to laser radiation compared with others due to larger band-gap (by means of multiphoton absorption) [97]. SiO_2 , with a bulk band-gap of ~ 9 eV, has the highest LIDT value. Al_2O_3 (~ 6.36 eV) has lower value followed by Ta_2O_5 (3,8-5,3 eV) and lastly Nb_2O_5 (3,1-4 eV).

Laser at nanosecond regime induces heat during the exposure to material as explained previously and the material starts to expand, which usually adds additional stress and the optical component breaks down. In this case, porous coatings should have a benefit over dense coatings. However, LIDT results revealed, that in most materials dense layers have higher resistivity to laser

radiation. One of the hypothesis is that porous structures creates more defects, therefore making them less resistive to laser radiation. Due to the porosity, coatings may absorb varies harmful particles including water from the environment lowering its resistivity to laser radiation. Additional experiments are needed to fully understand how porosity affects the LIDT values of single-layer coatings.

3.1.2. Main results and conclusions

This research enhances our understanding of how deposition parameters affect the optical and structural properties of thin film coatings deposited using GLAD method. By increasing the deposition angle in terms of vapor flux during GLAD process, the formation of single layer inner structure is modified.

Single-layer coatings of various materials (Nb_2O_5 , Al_2O_3 , Ta_2O_5 and SiO_2) were deposited at different angles (0° , 50° , 60° , 70° and 80°) using GLAD method. Due to shadowing effect, the porosity of these coatings increased with deposition angle. Although higher porosity can theoretically help reduce thermal stress, dense coatings exhibited greater resistance to laser-induced damage due to lower defect densities. Similar results were obtained by other research groups, who formed sculptured thin films [90], [91]. LIDT varied significantly among the materials – SiO_2 achieved the highest values ($>100 \text{ J/cm}^2$) at low deposition angles), Al_2O_5 maintained consistent resistance ($\sim 32.3 \text{ J/cm}^2$) regardless of porosity, while Nb_2O_5 and Ta_2O_5 exhibited lower resistivity, with porosity having minimal influence. Compared with other methods for single-layer formation, including sol-gel, where LIDT values reach around 20 J/cm^2 using 1064 nm wavelength laser system, our method has a very high potential [96].

The findings suggest that SiO_2 , with its high LIDT, is the most promising material for further research and application. However, the lack of a clear porosity correlation with LIDT values indicates that additional experiments are necessary to fully understand the complex relationship between structural properties and laser resistance.

3.2. The analysis of all-silica multilayer coatings

The LIDT of optical elements is a critical factor that has been extensively studied for many decades [94]. Several significant breakthroughs in coatings have increased the LIDT of optical elements, including thin-film band-gap engineering [98], E-field modification [99], and nano-structure formation [8].

In this work, we use the third approach to develop multilayer coatings for high intensity laser systems. The combination of nano-structured isotropic and dense layers formed using GLAD method allows the formation of optical elements using single material – in this case SiO₂. Previously we characterized silica single-layers to determine effective refractive indices at different deposition angles using „OptiLayer” software. In the next part a combination of multilayer structure consisting porous and dense silica will be deposited to form Bragg mirror for 355 nm wavelength.

The nanostructured film is considered as a low refractive index (1.25) layer deposited at 70-degree angle between the vapor flux and substrate normal. Dense film, formed at 0° angle, is considered as high refractive index (1.43) layer. Coating design consists of 53 QWOT layers with triple QWOT thin film of dense silica on top to strengthen the surface for cleaning purposes. The modelled E-field distribution and measured spectra of such mirror is showed in Figure 27 a) and b), respectively.

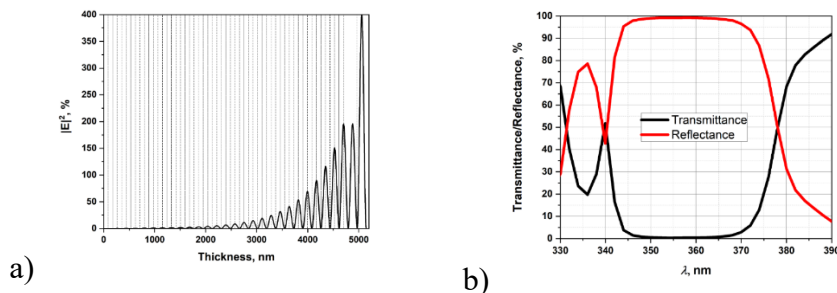


Figure 27. a) E-field distribution in the coating, b) transmittance and reflectance spectra.

The formation of mirrors using a single material, SiO₂, as one of the most optically resistive materials, has concerning drawbacks. Every second layer of the coating is highly porous and may absorb harmful particles from the environment including water, which adds some instabilities during optical characterizations. In order to observe spectral stability of such elements, three separate all-silica HR mirrors were fabricated with the same design. Spectrometric measurements were performed in different timescale after deposition process (see Figure 28). All three elements revealed a spectral shift, which is most likely induced by water absorption of porous layer, as the effective refractive index is changed. In Figure 28 d) a full spectra of second experiment is showed, in order to reveal how spectral shift are happening throughout the spectra for such coatings. As we can see, the spectra is shifting to shorter wavelength side.

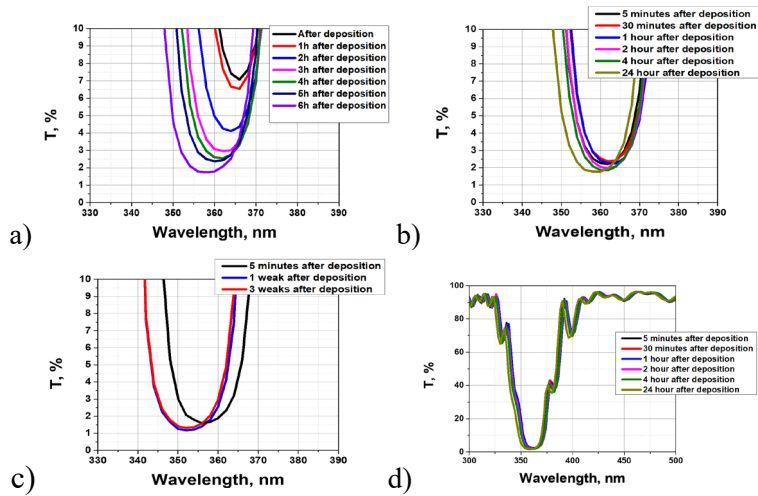


Figure 28. Spectral shift of all-silica mirrors a) first experiment, b) second experiment, c) third identical experiment and d) a full spectra of second experiment

Optical resistivity of these coatings was also measured using 1-on-1 method at 355 nm wavelength, 15 Hz repetition rate and 2.08 ns pulsed laser. Measurements were done three times – immediately after deposition process to avoid any degradation of coating, after 1 week and after 3 weeks when samples are exposed to open air environment. As shown in Table 1, coatings lack stability in terms of resistivity to laser radiation, with values consistently decreasing over time. Depending on time spent in open air environment, LIDT values may reach from up to 60 J/cm² [100] and decrease to 16 J/cm². Measuring LIDT immediately after deposition process gives different values, meaning that degradation can be higher or lower in different cases, also seen from spectral shift measurements. In Figure 29 optical microscope images are shown, where a) LIDT of the sample was measured immediately after deposition process, while b) is measured after 3 weeks. We observe different morphology of damaged spots. The mechanism of damage changes in all-silica mirrors as the coatings are stored in open air environment.

Table 1. LIDT results of all-silica mirrors.

Experiment nr.	LIDT, J/cm ²	LIDT after 1 week, J/cm ²	LIDT after 3 weeks, J/cm ²
1	35.3	35.3	16.0
2	56.8	52.6	19.4
3	80.2	62.9	18.6

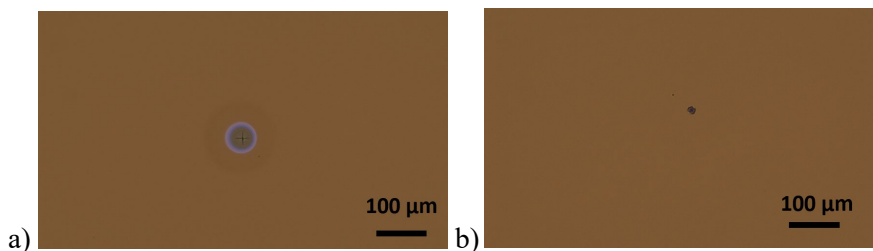


Figure 29. Optical microscope images of all-silica mirrors after LIDT measurement. a) Energy fluence of 82.4 J/cm^2 (measured at the same day as deposited) and b) energy fluence of 16.3 J/cm^2 (measured after several weeks)

During deposition process, formed layers are not fully oxidized, even if oxygen flow is used in the chamber. This leads to dangling bonds formation in the structure. The basic structural unit of vitreous SiO_2 is tetrahedron [101]. When ideal structure is formed, SiO_2 is stable, however it requires Si and O atoms to bind in specific length ($0.154 \text{ nm} - 0.169 \text{ nm}$) and angle (109.5°) [102]. In other cases, SiO_2 structure could be unstable and form various vacancies which affects optical element stability. It is impossible to deposit ideal structure coatings without any defects, however there are some reports how similar structures could be treated in order to stabilize optical and mechanical properties [103], [104]. In case of AR coatings formed by sol-gel method, one can expose silica films to ammonia treatment for a specific time to enhance optical and mechanical properties.

During coating formation by EBD technology, silica atoms are physically stacked without strong chemical bonding between them. The absence of strong chemical bonding is the main cause of instabilities of coatings. After water absorption, silanol groups are formed. While using ammonia treatment, condensation of silanol groups between the neighboring silica particles is induced and leads to strong chemical bonding between Si-O-Si groups.

In Figure 30 spectral changes are shown after all-silica mirror is treated with ammonia for 80 hours. Initially, spectra shift towards red spectral range, however remeasuring reflectance after six days, the spectra return to normal almost initial state. While ammonia treatment has an effect on all-silica coatings, instabilities remain.

It is known from the literature, that ammonia treatment can eliminate silanol groups and should increase porous coating mechanical and optical properties [103], [104]. The coatings spectral characteristics, which were treated by ammonia, changed only minorly, but there were no absorption visible. However, in our case, the ammonia treatment induced absorption in

all-silica coatings, indicating, that for multilayer coatings, this method is not that straight forward and needs more detailed analyzes.

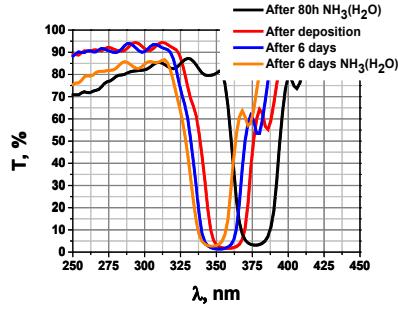


Figure 30. Transmittance spectra of all silica mirrors held in different environments

Raman scattering spectroscopy measurements were performed in order to obtain more deep information about all-silica coatings chemical structure (see Figure 31). Three all-silica mirrors were measured: 80 hours ammonia treated (blue), exposed to air environment (red) and isolated using desiccator (green). As expected, different stoichiometry bonds of silica are visible as well as silanol groups. Although all-silica mirrors were held in different environments, there is no significant difference found from Raman scattering spectroscopy. A presence of surface silanols and nonbridging oxygens are visible in measurement [105], [106], [107]. There are also visible D_1 band (four-membered rings) and D_2 band (three-membered rings), which remain constant for all samples [108], [109]. There are also some organic groups present, which could oxidize, leading to the formation of more silanol groups (H_2O , CO or CO_2) [110]. Demonstrated results are similar with the University of Rochester results, where they analyze similar porous structures [111].

LIDT measurements using 1-on-1 method were done for mirrors stored in desiccator twice (after 1 week and after 2 weeks) and for mirrors held in open air environment (after 2 weeks) (see Figure 32). Additionally, mirror held in air environment was annealed to 200° degrees for 1 h to see if there is some effect for optical resistivity [112]. From Figure 32 we can see that mirrors held in desiccator reached higher LIDT values ($\sim 42 \text{ J/cm}^2$) even after remeasuring after 2 weeks. Mirrors, which were exposed to air environment degraded and reached lower LIDT values ($\sim 18 \text{ J/cm}^2$), however the annealing of coating up to 200° degrees increased resistivity to laser radiation up to $\sim 39 \text{ J/cm}^2$. It seems, that all-silica coatings tend to absorb water from the environment, which affects their optical characterizations, however applying external heating treatment, optical performance may be refurbished. Usually, optical

elements are annealed to reduce absorption of elements, which increase optical performance [113]. Deposited metal oxide layers are not fully oxidized, thus heating treatment is applied at a certain temperature. In some cases, coatings are annealed after deposition in order to compensate film induced stress [114]. There are many reasons which could explain the increase of LIDT values for all-silica mirrors after annealing, however in this case, coatings even after annealing and again held in open air environment optical performance decreases. Additional experiments are needed to go deeper into understanding how porous coatings behave in different environments.

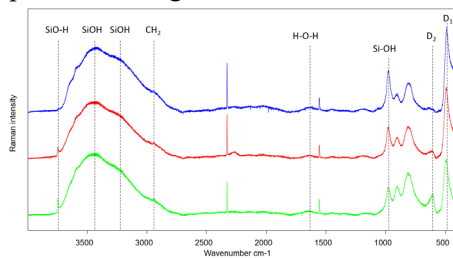


Figure 31. Raman spectra of all-silica mirrors held in air environment (red line), desiccator (green line) and ammonia for 80h (blue line)

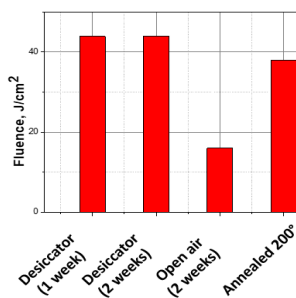


Figure 32. LIDT measurements of different samples treated differently (stored in desiccator, air environment and annealed)

3.2.1. The investigation of different environments for all-silica mirrors

In order to sustain optical characteristics of all-silica porous layers several isolations from air environment methods were tested. HR Bragg mirrors were deposited using same all-silica nanostructured coating design. We used desiccator and special, non-degradable polyethylene terephthalate glycol (PET-G) boxes to store coatings and fill with different gasses: oxygen, argon and nitrogen. All samples were held for 2 weeks, while LIDT 1-on-1 measurements were performed each week (see Figure 33). Immediately after LIDT measurement, mirrors were stored back to its environment to minimize exposure to air environment as much as possible. The results are extremely promising, especially samples held in argon and nitrogen gasses, when LIDT

values reached up to $\sim 100 \text{ J/cm}^2$ after one week. In other environments we can see good results as well: LIDT of samples held in oxygen environment values reach $\sim 50 \text{ J/cm}^2$, in desiccator $\sim 80 \text{ J/cm}^2$ and in no gas environment values are $\sim 28 \text{ J/cm}^2$. Although all-silica mirrors were returned to their initial environments immediately after LIDT measurement (measurements were done in open air environment), from the second measurement we can see degradation in all cases. LIDT values drops to $\sim 80 \text{ J/cm}^2$, $\sim 65 \text{ J/cm}^2$, $\sim 23 \text{ J/cm}^2$ and to $\sim 55 \text{ J/cm}^2$ when samples are held in argon, nitrogen, oxygen and desiccator environments respectively. During mirror exposure to air environment, harmful particles may have been absorbed to porous layers, decreasing resistivity to laser radiation of optical elements.

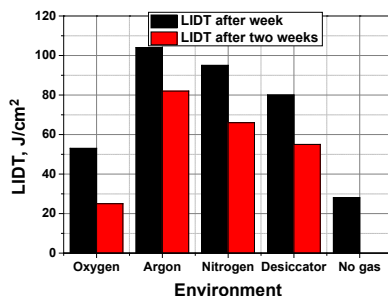


Figure 33. Histogram of LIDT in different environments

In Figure 34 1-on-1 LIDT measurement damage probability depending on energy fluence of all-silica mirror held in Pet-G box, but without any gasses. We can see that even if some spots were damaged at relatively low energy (20 J/cm^2), some spots were able to withstand more energy showing the potential of these coatings. After analyzing some damaged spots with Nomarski microscope (see Figure 35) and AFM (see Figure 36) we can see that damage were initiated by defects, which is expected in EBD coatings.

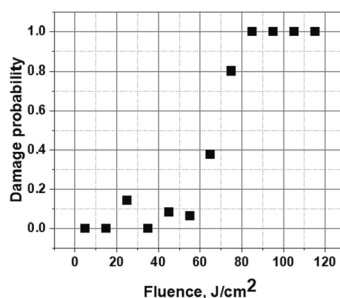


Figure 34. The resistance to laser radiation of HR all-silica mirror held in PET-G box

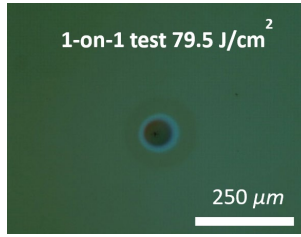


Figure 35. Optical microscope image of damaged spot using 75.5 J/cm^2 1-on-1 test

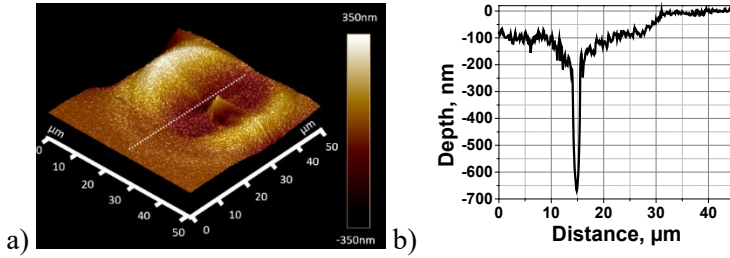


Figure 36. a) AFM image of damaged spot using 75.5 J/cm^2 1-on-1 test and b) profile of damaged spot

1-on-1 LIDT measurements revealed extremely high potential of all-silica mirrors in terms of resistivity to laser radiation in different environments, however degradation effect is still the major issue. To implement such coatings in laser systems, the degradation problem must be resolved. One of the proposals would be to seal the laser system from environment and fill it with argon or nitrogen gasses to reduce degradation effect, but it is unclear how long mirrors could sustain their optical characteristics. Another proposal would be to use additional ex-situ actions such as external heating to regain original resistivity of all-silica mirrors as the degradation process is not long term as seen from Figure 32.

3.2.2. Local laser irradiation annealing of multilayer sculptured coatings

Material related to this chapter was published in [A1] and [C4, C5]

After initial 1-on-1 LIDT measurements, fully degraded all-silica coating exhibit $\sim 14.7 \text{ J/cm}^2$ threshold value with zero probability of damage and may increase up to 65 J/cm^2 , with the probability of damage up to 50 % [10], [115]. Similar coating formed by IBS technology using hafnia/silica materials exhibit 20 J/cm^2 to 30 J/cm^2 with the damage probabilities of 0 % to 50 %, respectively [10]. Coatings formed by IBS technology has a lower defect density compared to EBD technology, however further improvements in terms

of LIDT is limited by high refractive index material – hafnia, and high stress values. Although mostly EBD coatings LIDT is limited by defects [116], in case of all-silica we can see different type of degradation related with absorption of harmful particles from the environment.

Local laser irradiation annealing (LLIA) method was applied in order to restore and even increase optical performance of all-silica mirrors after porous coating is exposed to open air environment [49]. After first measurement, we registered values up to 180 J/cm^2 , which optical elements were able to withstand, however it wasn't completely stable. More extensive experiments are needed to explain why and how exactly this LLIA works in nanostructured coatings.

Different LLIA protocols were applied to increase all-silica mirrors optical performance. Initial fluence started from 10 J/cm^2 (fluence energy selected after 1-on-1 LIDT evaluation) and was increased with a certain increment per pulse speed (see Figure 37). In Figure 38 series of experiments with different increment per pulse is demonstrated, where “*” marks damage, which occurred during exposure to laser radiation. From the experiments, we can divide results to three regions: when we have a very fast increase of fluence energy ($32 - 4 \text{ J/cm}^2$ per pulse) we have no conditioning – optical elements can withstand $50 - 80 \text{ J/cm}^2$. As the increment per pulse is reduced to $4 - 0.25 \text{ J/cm}^2$ per pulse we have semi conditioning region where optical elements reach values from 50 J/cm^2 up to 180 J/cm^2 . Finally, when fluence energy increment per pulse is reduced to $0.25 - 0.125 \text{ J/cm}^2$ per pulse we have conditioning region, where all-silica mirrors reach values up to $180 - 200 \text{ J/cm}^2$. These results show extreme potential of all-silica mirrors to withstand extremely high energy fluences using nanosecond laser pulses. To our knowledge, the highest LIDT values reached in pulsed ns regime using 355 nm wavelength laser system is 90 J/cm^2 for bulk silica material [117].

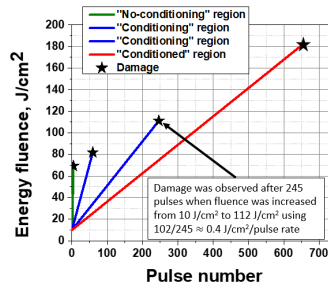


Figure 37. An example of LLIA by ramping the fluence at different rates

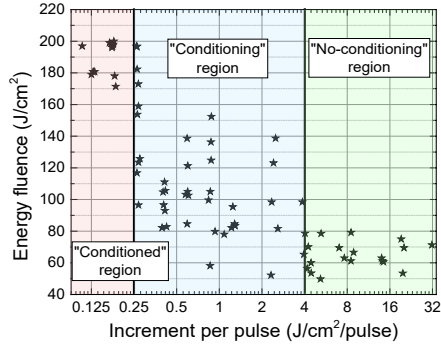


Figure 38. LIDT results of all-silica mirrors using LLIA at different fluence increments per time

For further investigation, longevity of the coatings were tested using LLIA rate of 0.125 J/cm^2 per pulse. In Figure 39, we can see 4 different LLIA experiments where energy fluence is raised to a certain value and is fixed for a longer time, however we noticed, that after a while coating got damaged. It is unclear if the fatigue effect [118] is responsible for element breakdown or we encounter other issues. Following experiment was done to determine energy fluence at which all-silica mirrors can withstand at least 10000 pulses without any damage using LLIA with rate of 0.125 J/cm^2 (see Figure 40). The highest energy fluence registered was 174 J/cm^2 for 10000 pulses without any damage observed on coating surface. Energy fluences used above this value damaged coating after certain pulse number.

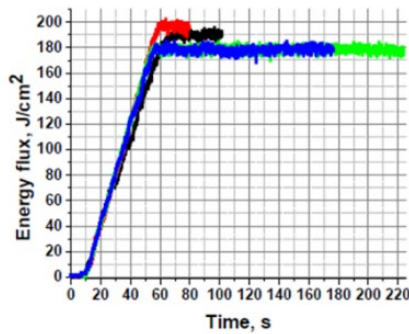


Figure 39. LLIA results using 0.125 J/cm^2 increment per pulse

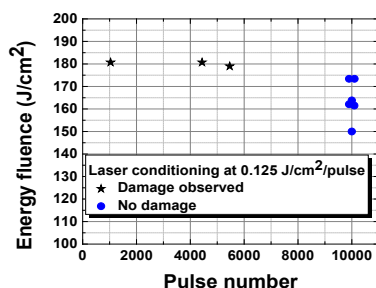


Figure 40. Optical resistivity of all-silica mirrors after the LLIA and 10000 shots

Morphology of damaged spots were investigated using Nomarski microscope to understand the origin of damage (see Figure 41). When coating is damaged using energy fluence up to 200 J/cm², the large crater is seen in the area covering any possible defect-based precursors. It is worth mentioning, that it is impossible to stop laser system immediately after it gets damaged, so several pulses still hit the same spot after initial destruction occurs.

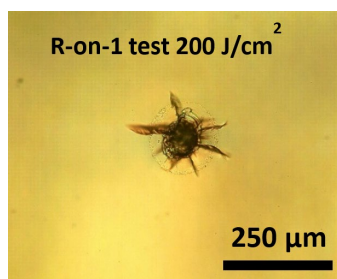


Figure 41. Nomarski microscope images of R-on-1 and 1-on-1 LIDT tests of all-silica mirrors

Several hypotheses were raised in order to explain why all-silica mirrors are able to withstand such high energy fluences by using LLIA. When using nanosecond laser pulses, thermal expansion effect and stress related damages usually occurs in optical coatings [119]. All-silica coatings are highly porous (50 % porosity for porous layers and 10 % for dense layers), which exhibit low stress [83] and the inner structure is able to expand without any damage during exposure to laser radiation. Residual stress was measured for these mirrors using white light interferometer and evaluated stress reached 84 MPa. Absorption was also measured (see Figure 42), which reached 4 – 12 ppm at 355 nm wavelength indicating very low absorption.

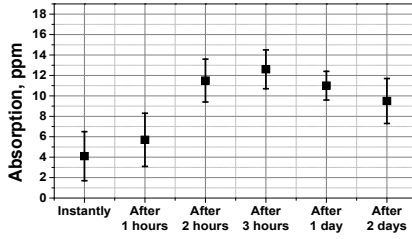


Figure 42. Absorption of all-silica mirror using LID method per time

It is difficult to figure out the main reason, why LLIA improves all-silica mirrors optical performance. As the porous coating degrades in air environment absorbing various harmful particles it forms silanol groups, there are many precursors stuck inside all-silica structure, which may initiate damage in coating when high power laser radiation strikes. As the precursors absorb high energy pulses, they heat and because of the high pressure created inside the structure, it explodes. However, if we increase laser energy slowly with the beam spot diameter of $61\ \mu\text{m}$, it is likely that the precursors will gradually move out of the area of impact to the outer space surrounding porous layers. This is only a hypothesis, which is partially confirmed by our studies including degradation during time (see Figure 44).

In order to support this claim, a longevity was tested and analyzed in Figure 44. The experiment consists of 7 steps which were made at the same spot of the sample. All-silica mirror was locally irradiated using the same ramping rate of $0.125\ \text{J}/\text{cm}^2$ per pulse to an energy fluence of $160\ \text{J}/\text{cm}^2$ as a first step. For other steps irradiation was continued and stopped with the same energy but different time intervals. When time of laser radiation being stopped reaches 100 s and more (6th step), the damage is initiated after turning the laser on again, indicating that damage precursors are returning. This experiment was repeated several times with always with the same outcome. When energy fluence is raised to $160\ \text{J}/\text{cm}^2$ at one spot and the laser is turned off for 100 seconds or longer, all-silica mirror gets damaged after turning the laser on again with the same $160\ \text{J}/\text{cm}^2$ energy fluence at the same spot. Typically, conditioning effect is an irreversible phenomenon, which clears defects in band gap region permanently increasing resistance to laser radiation of optical element [49], [50], [51]. It is clear, that standard explanation which is used for dense layers cannot be applied to porous structures as gasses or humidity can easily diffuse through nano size gaps within the exposed to laser radiation area.

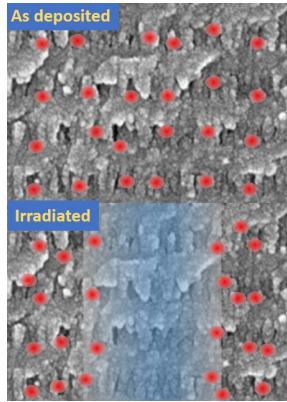


Figure 43. Principal idea of LLIA using long multipulse regime: red circles represent the defects (gases or humidity) and transparent blue cylinder – interaction area with laser radiation

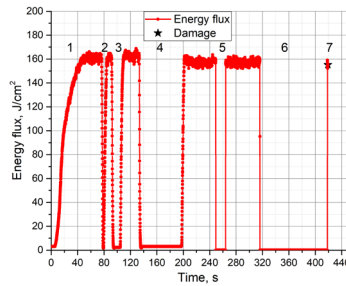


Figure 44. Longevity of LLIA all-silica mirrors

Up till this point, LLIA and LIDT measurements were done using 61 μm diameter laser radiation, however, in most laser systems, the used diameter is wider. The diameter was increased to 200 μm and LIDT and LLIA was remeasured for all-silica mirrors to compare results. 1-on-1 LIDT results are shown in Table 2, where three different spots were measured on the sample. We observe a slightly lower LIDT values when beam diameter is approximately 200 μm , compared with 61 μm diameter.

Table 2. 1-on-1 LIDT results of all-silica mirrors using different laser beam diameters.

Experiment nr.	LIDT (61 μm diameter), J/cm^2	LIDT (200 μm diameter), J/cm^2
1	16.1	10.5
2	14.3	9.7
3	15.2	9.8

LLIA was applied to all-silica mirrors with increased beam diameter as shown in Figure 45. The energy fluences, which mirror could withstand were lower reaching from 60 to 90 J/cm². At the moment, we do not have an explanation for this and further investigation must be done.

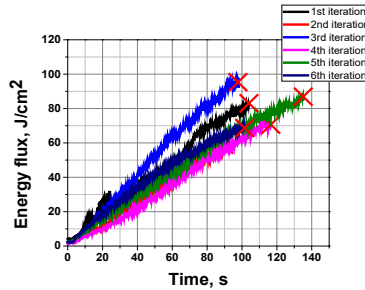


Figure 45. LLIA results with laser beam diameter of 200 μm

3.2.3. Investigation of different environments using local laser irradiation annealing

For further investigation of all-silica mirrors, LLIA was tested in different environments to see if the effect remains the same. To begin with, samples were thermally heated up to 80° C for spectral analysis (see Figure 46). Both samples (GLAD sample 1 and 2) exhibit similar spectral shift of up to 10 nm to shorter wavelength, while typical hafnia/silica EBD mirror (E-Beam) reach up to 3 nm spectral shift and hafnia/silica IBS mirror (IBS) doesn't change. Due to high porosity in EBD coatings, particularly in GLAD nanostructured coatings, after applying external heating, water is evaporating from layers reducing effective refractive index, indicating the shift to shorter wavelength of spectra. After optical elements are returned to ambient environment, spectra return to its original state depending on the humidity, meaning that heating does not apply any permanent changes. Similar behavior is observed when placing optical elements under vacuum (see Figure 47). All-silica coatings under high vacuum exhibit stronger spectral shift then thermally induced shift (up to 16 nm), indicating lower humidity in vacuum chamber rather than in 80° furnace.

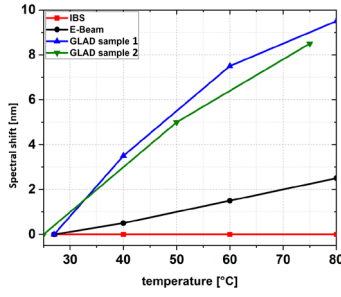


Figure 46. Coatings spectral shift initiated by temperature

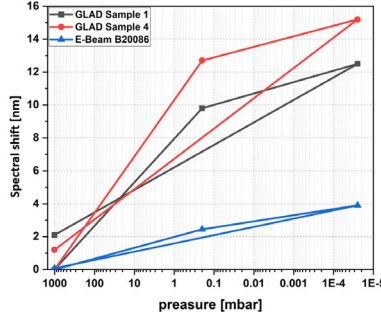


Figure 47. Coatings spectral shift initiated by vacuum

LLIA experiments were done in Laser Zentrum Hannover, where samples were tested using 355 nm wavelength, 100 Hz, beam diameter 115 μm , 5.3 ns pulsed Nd:YAG laser system. All samples were stored in glass box, where environment conditions were changed: normal conditions (at air room temperature), air environment at 70°, argon atmosphere at room temperature and argon atmosphere at 70°. LLIA was slightly different: after 1000 pulses at specific fluence, samples were inspected, if there were no visible contamination or coating damage spotted, energy fluence was increased by 2 J/cm² and the process was repeated at the same spot until damage occurred.

In air environment at room temperature, results are similar (around 140 J/cm²), although because of the different measurement routine (inspection of sample after 1000 shots) it was expected for values to differ (see Figure 48). When external heating is applied to 70° temperature in air environment, resistivity to laser radiation drops by 71 % to 39.5 J/cm². After all-silica samples were stored in argon gas environment, at room temperature resistivity to laser radiation dropped by 52 % to 68.5 J/cm² and after additionally applying external heating to 70° - LIDT dropped to 35.2 J/cm². The experiment was repeated 4 times for 10 different spots placing samples in different order. However, the results remained the same, indicating, that heating did not apply any permanent changes.

Analyzing previous results, we observed spectral shift change when heating was applied due to water leaving the porous layers. The initial thought was, that LLIA effect would be enhanced by additional external heating for the same reason, however results are opposite. In order to try to explain the reason, SEM and Nomarski microscope images were done (see Figure 49). Morphology of damaged areas in air or argon gas environments at room temperature looks very similar and it is typical as we can see defect-initiated damage. When we analyze morphologies of damaged spots when external heating was applied, from SEM image we can see that inner structure cracked, while only a small spot is visible from optical microscope image. Such cracks are stress related damage sites, which are observed in IBS coatings [120].

As the temperature of the Bragg mirror rises, it will experience thermal expansion, which can introduce mechanical stress into the mirror's structure. This could lead to optical distortions, affecting the beam quality and further lowering the LIDT. The stress might also degrade the integrity of the coatings, making them more susceptible to LIDT. The long interaction time of a nanosecond pulse increases the chances of thermal gradients developing in the material. This is probably what happened in our case, after heating up the coating, thermal-induced stress appeared lowering the resistivity of all-silica mirrors. Similar results were obtained when analysing single-layer optical coatings with different pulse durations [121]. The temperature has minimum effect for LIDT when using 2 ps or shorter pulses, however, when the pulse duration is 200 ps or longer, the LIDT values of all coatings drops with the increase of temperature.

When comparing two different environments – argon and air, the LIDT value drops by 52 %. This might have happened because argon gas has lower thermal conductivity compared to air. This means that in an argon environment, heat will dissipate more slowly from the Bragg mirror during high-intensity laser exposure, potentially causing localized heating and increasing the likelihood of damage. The temperature will rise more quickly in the material resulting in a lower LIDT value. Previously we have done some experiments by storing all-silica mirrors in argon gas environment and it helped to reduce degradation effect, meaning that this environment should have a positive effect to Bragg mirrors in terms of LIDT. However, it seems that when LIDT measurement is applied in argon gas environment, it has negative effect on the value.

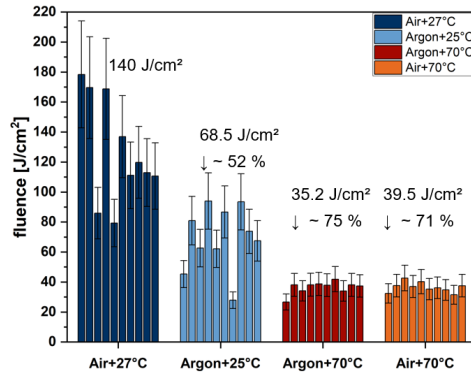


Figure 48. LIDT measurements of all-silica mirrors at different environments and with temperature treatment

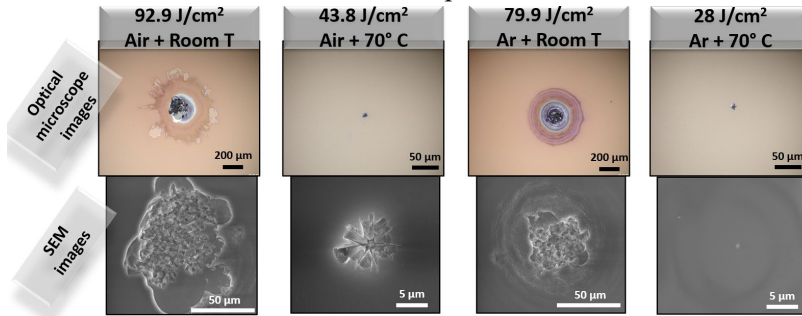


Figure 49 Optical microscope and SEM images of damage morphologies achieved in different conditions (air and room temperature, air and 70° C temperature, argon (Ar) gas and room temperature and argon gas and 70° C temperature)

3.2.5. Main results and conclusions

All-silica multilayer coatings were developed using GLAD with a combination of dense and porous SiO₂ layers. The research demonstrates the potential of nano-structured all-silica coatings for high-LIDT applications. Porous-dense multilayer structures, fabricated using GLAD, achieved significant resistance to laser-induced damage ($\sim 80 \text{ J/cm}^2$) under controlled conditions (argon or nitrogen gas environment). However, environmental exposure remains a challenge, with water absorption and stress-related damage being major factors in performance degradation. To compare with other optical elements, the LIDT value is not more than 15 J/cm^2 when using 355 nm wavelength, nanosecond pulsed laser [122].

Local laser irradiation annealing emerged as a promising technique to enhance LIDT by conditioning the porous layers (up to $\sim 180 \text{ J/cm}^2$), clearing

defects, and stabilizing the optical response. External heat treatments and controlled gas environments were applied in order to further improve optical coatings, however it introduced complexity and achieved LIDT values were lower. There are no other mirror elements in the world, which demonstrated similar results.

The findings highlight critical areas for improvement, including sealing porous structures from environmental interaction and refining post-deposition treatments like LLIA. These advancements will be pivotal for applying such coatings in high-power laser systems. Future studies should focus on understanding the long-term degradation mechanisms and optimizing protective strategies to ensure sustainable performance.

3.3.1. Enhancement of HR mirrors using sculptured thin films

The resistance to laser radiation of an optical element depends on several extrinsic factors including defects, inhomogeneities, light absorption, etc. However, after elimination of these extrinsic sources, LIDT is limited by intrinsic property of the coating, which is bandgap energy of layer materials. As mention previously, standard multilayer optical coatings are fabricated using high (H) and low (L) refractive index materials. Therefore, the H is the weakest link of multilayer coating with the lowest bandgap energy.

Meanwhile, all-silica mirrors show high potential in terms of LIDT value, but low refractive index contrast between porous and dense layers forces a drastic increase in the number of layers needed to achieve high reflectance. As a consequence, such multilayer coatings suffer from scattering losses, especially in UV wavelengths, and, as mentioned before, are highly sensitive to environmental changes. To overcome these issues, it was proposed to make a hybrid multilayer stack using two deposition techniques – IBS and GLAD [10]. Such optical coating showed promising results in the publication, however LIDT data revealed that damage probability at 0 % of upgraded element is twice lower compared to IBS coating, although damage probability at 50 % is enhanced up to 4 times. Similar results are obtained in previous section of all-silica mirrors, however LLIA may be applied to increase these values.

We coated a standard IBS mirror for 355 nm wavelength using tantala and silica materials and then deposited an additional 4, 10, and 16 layers of all-silica multilayer structure (see Figure 50). Such coatings exhibit no spectral shifts, when placed in different environments, since the base is formed from dense IBS layers.

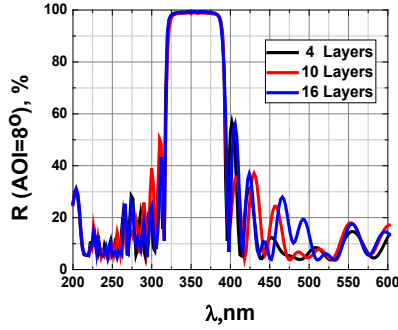


Figure 50. Reflectance spectra of mirrors at 355 with different number of all-silica layers

LIDT measurements were performed using the same nanosecond pulsed laser system at 355 nm wavelength. As expected, such mirrors have relatively low LIDT values (up to 7 J/cm²) and upgrades doesn't have any effect for 1-on-1 LIDT test measurement at 0 % damage probability (see Figure 51). Next step was to check if LLIA has an effect for such optical coatings. The IBS mirror had no effect as the damage always occurred at the same fluence energy. However, even with a 4-layer upgrade we observe an improvement in the resistance to laser radiation (see Figure 52). Resistivity of optical element was enhanced up to 14 J/cm², 40 J/cm² and 47 J/cm² when IBS mirror was coated by 4, 10 and 16 layers of all-silica, respectively, using LLIA method. These results show great promise for optical coating fabrication by combining two technologies to increase the overall LIDT of the element. Such optical component has low scattering and spectral shifts with the change of environment.

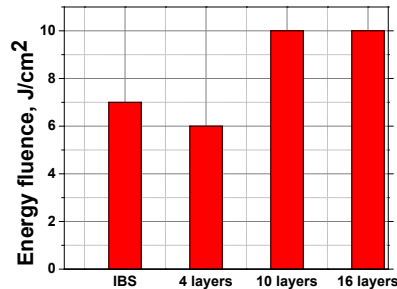


Figure 51. 1-on-1 LIDT measurements of each sample

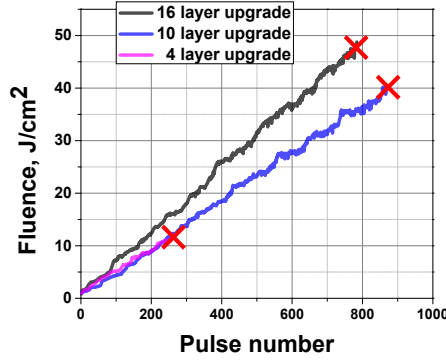


Figure 52 LLIA measurement of upgraded mirrors with different number of all-silica layers. Red cross marks the fluence energy at which element is damaged

3.3.2. Application of sculptured thin film optical elements in femtosecond lasers

In previous section, all-silica coatings for nanosecond pulsed laser were analyzed. The main limiting factor in such optical elements is the presence of defects, which absorb the laser beam and leading to damage of the exposed areas. When the laser pulse duration is shorter (<10 ps), the bandgap energy becomes a critical factor for optical elements.

Theoretically, all-silica mirrors should exhibit very high LIDT values used with fs pulsed laser systems due to silica's wide bandgap, which minimizes the influence of defects. In this section, we conducted experiments with three different mirror designs: standard 11-layer hafnia/silica IBS coating, the same IBS mirror with 8 layers of all-silica on top as an upgrade and an all-silica mirror for 800 nm wavelength at a 45° angle of incidence (see Figure 53).

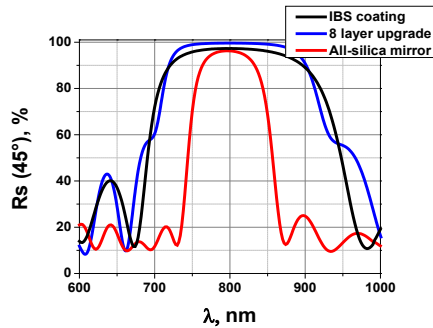


Figure 53. Reflectance measurements at 45° angle of incidence.

LIDT measurements were performed at ELI Beamlines for all 3 elements using 37 fs pulsed laser system with a beam diameter of 120 μm . R-on-1 (Ramping test) using relatively slow and fast energy fluence increase, 100-on-1 and 100-on-1 with bigger beam diameter (160 μm) measurements were done. In Figure 54 we can see, that all-silica mirrors did not perform so well as expected, although in most cases the LIDT value were slightly higher compared with other elements. In all cases, typical IBS coating had lowest LIDT value.

One of unexpected results was the difference in LIDT values between slow and fast R-on-1 measurements of all-silica and upgraded mirrors. In both cases, using fast energy fluence increase, the optical element withstood higher laser radiation values, which is completely different from using nanosecond pulse duration laser systems. It is clear that the conditioning effect plays no role in this specific case, although there are some speculations about optical element fatigue effects. Fatigue effect in optical elements exists due to the heat accumulation and defect incubation effects leading to damage at the exposed area [123].

Another interesting observation was the increase in LIDT values when the beam diameter was increased from 120 μm to 160 μm during 100-on-1 measurement. Normally, as the beam diameter increases and more surface area is exposed, there is a higher chance of hitting a defect or other impurities on the optical element; however, in this case the LIDT increases. At the moment we don't have an explanation and additional measurements are needed.

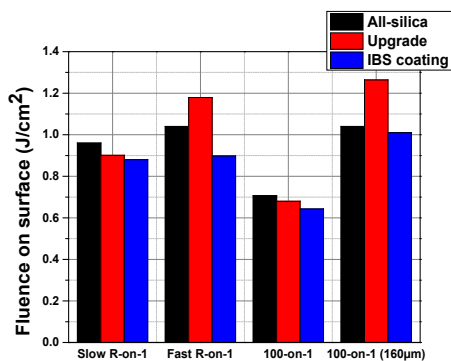


Figure 54. LIDT measurements of mirrors (R-on-1 with slow and fast energy increase and S-on-1)

Additionally, 1-on-1 LIDT measurement (with 120 μm beam diameter) was done for upgraded mirror in order to analyze damaged spots at LIDT using confocal microscope. It is extremely hard to detect damage during measurement, thus after damage occurs, additional pulses hit that spot and drills more into the coating. In Figure 55 laser irradiated areas are shown using different energy fluences. 1-on-1 LIDT measurement values are higher compared to S-on-1, because these are considered as intrinsic, while multi-pulse test method evaluates fatigue/accumulation effects.

Although ablation of coating is visible at 1.15 J/cm^2 energy fluence, we can observe some color changes at lower energy levels, which may be a precursor to catastrophic damage at higher fluences or longer exposure. Discoloration indicates a structural modification within the volume of the material, which in theory is considered as a damaged spot, since it is an irreversible process [124].

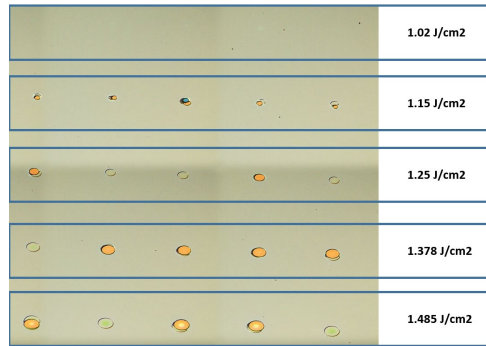


Figure 55. Image of upgraded mirror after 1-on-1 measurement

The catastrophic damage was analyzed in more detail (see Figure 56) to determine which layers were ablated from the coating. Most of the damaged areas are 0.18–0.35 μm deep, indicating that the second layer (which is porous silica layer) was damaged. When higher energy fluence is used, the depth increases to 0.65 μm or 1.018 μm , which correspond to the 4th and 6th layers, both of which are also porous. From the experiments, it is clear, that porous silica layer is less resistant to laser radiation when using fs pulsed lasers. However, the reason for the lower LIDT values of nanostructured layers remains unknown and requires further analysis and experiments.

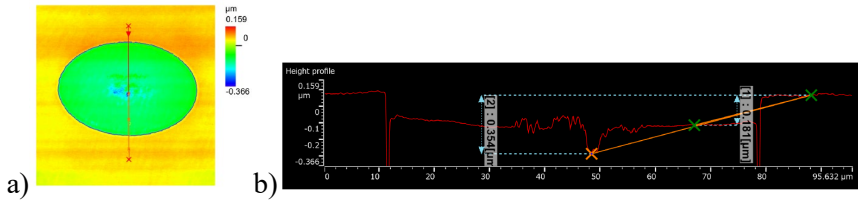


Figure 56. a) Nomarski microscope image of damage spot at 1.15 J/cm^2 and b) profile depth of damaged spot

3.3.3. The main results and conclusions

Hybrid multilayer coatings combining IBS and GLAD techniques were investigated to improve LIDT. Enhanced resistivity was demonstrated, with LIDT values reaching up to 47 J/cm^2 for hybrid all-silica mirrors after LLIA. This technique effectively combined low-scattering and high-resistivity layers.

All-silica coatings, standard IBS coatings and same IBS mirror with 8-layer upgrade (all-silica) on top were tested for femtosecond laser systems. Upgraded IBS optical element achieved higher LIDT values compared to traditional IBS coatings. However, unexpected fatigue effects and structural vulnerabilities were observed, particularly for nanostructured porous silica layers. To compare results, with other groups, using similar laser system, high quality IBS coatings may reach up to 1.3 J/cm^2 using R-on-1 LIDT protocol [87].

This research advances the field of optical coatings by demonstrating the potential of hybrid multilayer coatings combining GLAD and IBS techniques for high-power laser systems in nanosecond and in femtosecond regimes.

4.1. Coatings on crystals

4.1.1. All-silica coating on YAG crystal

In modern laser systems, doped crystals are the most popular material for the generation of pulsed laser light. Therefore, a lot of focus is directed at preprocessing crystals in order to maximize output laser power. All optical elements experience Fresnel reflections, so it is necessary to deposit AR coating on the crystal surface to avoid intensity losses. LIDT of coated crystal surfaces is dependent on surface quality, preprocessing with etching or polishing, which also impacts adhesion between coating and crystal [32]. Conventional techniques use high and low refractive index materials for AR

coating formation. However, high refractive index material reduces the optical element's LIDT. A promising alternative is a nanostructured all-silica coating directly deposited on crystal as a highly resistive material to minimize Fresnel reflections and retain high LIDT values.

All-silica coating was deposited directly on a YAG crystal to analyze the benefits of nanostructured coatings. Before deposition, one YAG crystal was plasma etched to improve surface quality and increase LIDT [125]. As mentioned before, the LIDT of a crystal is also influenced the crystal's surface preprocessing. To negate this factor and analyze only the coating, HR mirror was deposited at 532 nm wavelength directly on the YAG crystal (see Figure 57). The coated YAG crystal was also analyzed at a 45° angle of incidence, where reflection was much lower, simulating how AR coating might behave.

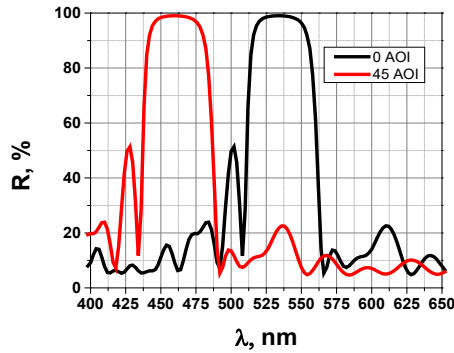


Figure 57. Reflectance spectra of all-silica mirrors at 0° and 45° AOI

Surface quality of YAG crystals was evaluated using a microscope with different magnification before (see Figure 58) and after all-silica coating deposition (see Figure 59 and Figure 60). Microscope images reveal some defects left on the YAG crystal surface after the plasma etching process and that these defects became significantly more prominent compared to the unetched YAG crystal. Both crystals were coated in the same process. Perhaps, defects were more visible because of the HR coating at 532 nm, so making it easier to spot them, meaning that plasma etching introduces defects on the crystal surface reducing the overall quality of the element. Most likely, plasma etching exposed subsurface polishing particles, making defects on the YAG crystal surface more evident.

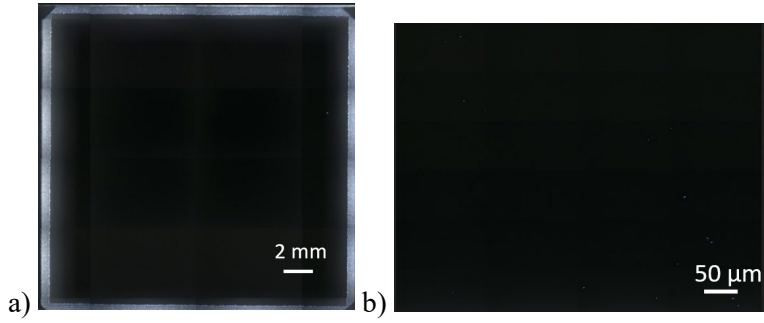


Figure 58. Optical microscope image of uncoated etched YAG crystal a) 5x, b) 20x magnification

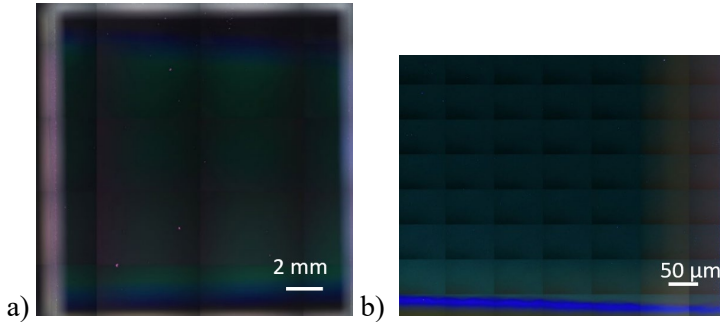


Figure 59. Optical microscope image of unetched coated YAG crystal a) 5x, b) 20x magnification

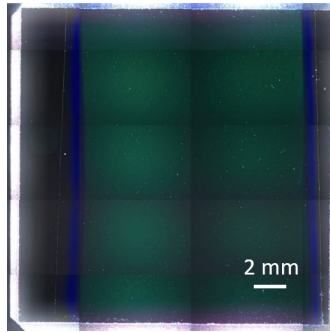


Figure 60. Optical microscope image of plasma etched coated YAG crystal

After surface inspection, coated YAG crystals were tested using the same nanosecond laser system at the second harmonic (532 nm wavelength, ~ 3 ns, 80 μm diameter). Initially, 1-on-1 measurements were performed at 45° angle of incidence (see Figure 61). At this angle, the Bragg mirror was shifted to shorter wavelengths, leaving transmittance at 532 nm around 85 %, which imitates AR coating. As expected from microscope measurements, coating on the etched YAG crystal exhibits significantly lower resistance to

laser radiation (1.56 J/cm^2 up to 83.6 J/cm^2) compared to the unetched YAG crystal (13.5 J/cm^2 up to 29.6 J/cm^2). At 45° angle of incidence, transmittance was present throughout the element, so any defects induced during YAG crystal surface etching greatly affected LIDT. However, whenever laser radiation was not hitting defects, etched YAG crystal reached almost 3 times higher LIDT value. Thus, with proper polishing and plasma-etching, it is possible to achieve a YAG crystal with a nanostructured all-silica coating that demonstrates high resistivity to laser radiation.

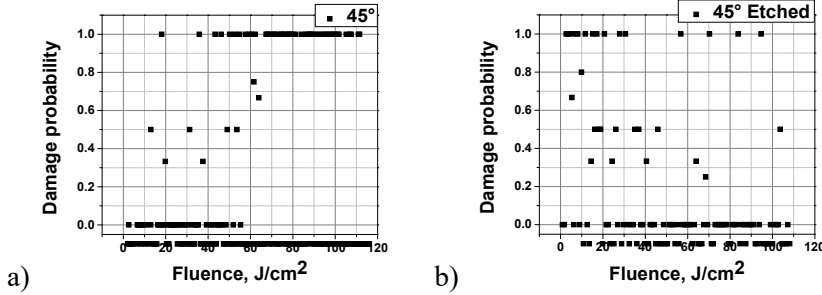


Figure 61. LIDT measurement of a) unetched, b) etched YAG crystal at 45° AOI

Following experiments included 1-on-1 LIDT tests at a 0° angle of incidence. In this case, the setup featured a HR mirror, which reflects 99 % laser radiation. Plasma-etched YAG crystal exhibit a 66 J/cm^2 LIDT value (see Figure 62), meanwhile unetched YAG crystal achieved maximum laser fluence energy up to 222 J/cm^2 without any damage spots. Laser beam did not penetrate through the surface of the all-silica coating; however, the plasma-etched YAG crystal surface had a lot of defects, which are probably larger than $3 \mu\text{m}$ and the coating was not thick enough to cover them. After laser radiation interaction with the optical element, there was a high chance of hitting a defect, thereby damaging the exposed area. From Figure 63 we can see that damage is initiated by defects on the surface. LLIA was utilized on the plasma-etched YAG crystal at a 0° angle of incidence, to see if it could enhance the LIDT value (see Figure 64). It reached 140 J/cm^2 , however, at higher fluence energies, the element broke due to defects on the surface.

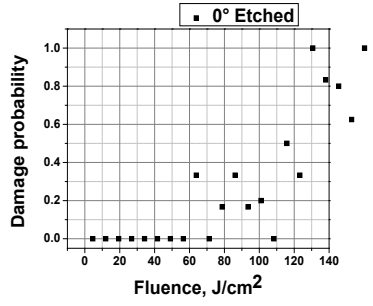


Figure 62. LIDT measurement of etched YAG crystal at 0° AOI

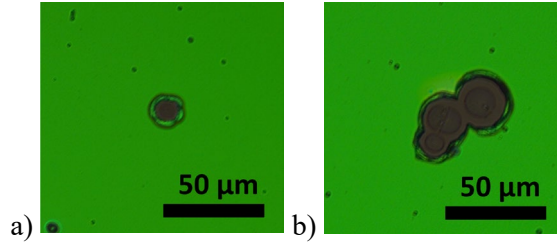


Figure 63. Microscope images of etched YAG crystal surface after 1-on-1 LIDT measurements at a) 66 J/cm² and b) 75 J/cm²

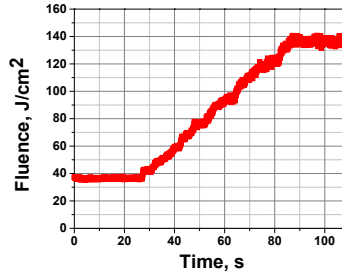


Figure 64. Local annealing of etched YAG crystal at 0° AOI

4.1.2. Total internal reflection in YAG crystals

Material related to this chapter was published in [A2]

In previous chapter, we showed how nanostructured coatings can be used in microlaser systems by depositing porous layers directly on laser crystals. However, porosity has some disadvantages, including degradation during time due to water absorption, which reduces the resistivity of the optical element and introduces spectral shifts. Although LIDT issue can be solved by applying the LLIA effect, precise spectra in most laser systems are required. Nevertheless, there are unique coating designs, in which low refractive index layers are required to achieve specific spectral performance. Using

nanostructured layers, we can aim to increase the angle range at which TIR effect occurs. TIR effect is required for a slab-type gain module, which consists of a YAG crystal and two cooling blocks (see Figure 65).

Complex spectral requirements for the coating must be addressed during the development of TIR coating on the YAG crystal. To avoid thermal lensing and birefringence, coatings that initiate TIR must be combined with cooling blocks. The aim of a nanostructured coating is to increase angle at which TIR still occurs. Using dense silica layers, it is possible to gain TIR at a 55° angle of incidence, however, using porous silica layers we can reach 45° .

Although, the required effect is achieved using only GLAD coatings, additional spectral characteristics are required for the final system. The pumping laser (at 800 nm wavelength) is directed from the top of the YAG crystal (S1 in Figure 65), when traveling inside the crystal it hits the surface on which the GLAD coating is deposited (S3). To increase the pumping effect of laser, the surface has to be reflective at a 790 – 820 nm wavelength, with a $0 - 25^\circ$ angle of incidence for it to bounce back through the YAG crystal again. During laser pumping, additional generation of 1064 nm laser radiation is induced, which hits the YAG crystal surface at $0 - 10^\circ$ angle of incidence. This laser radiation is considered as parasitic radiation, therefore, high transmittance is needed to guide this radiation away from the crystal. Lastly, everything is covered with thermal paste, which is cooled down. To achieve such spectral characteristics, additional coating is applied using IBS or EBD methods.

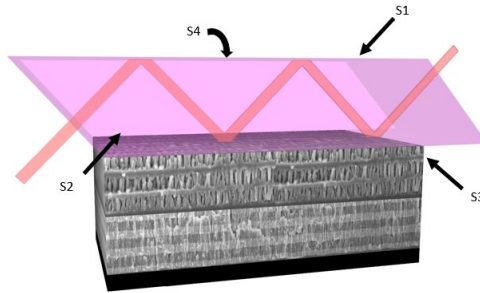


Figure 65. Principal scheme of YAG crystal where S1 is top side, where pumping laser is directed, S2 and S4 sides are covered with thermal paste for cooling and S3 is coated with hybrid coating for TIR

The most difficult part is to achieve TIR at 1064 nm for both polarizations at 45° AOI. If the angle of TIR is higher, it requires longer crystal. Moreover, GLAD coatings are known to have high LIDT values. Therefore, the proposed multilayer structure has a high potential.

In order to achieve high reflectivity in multilayer interference coating, high refractive index contrast between layers and having high number of layers are needed. It can be described by Fresnel coefficient expressions. However, as the AOI increases, formula must be transformed by changing refractive indices to certain expressions, which include the AOI and are called effective refractive indices [126], [127].

$$\hat{n}_1 = n_1 \cos \alpha_1 = \sqrt{n_1^2 - n_0^2 \sin^2 \alpha_0}, \quad \text{for S polarized light} \quad (13)$$

$$\hat{n}_1 = \frac{n_1}{\cos \alpha_1} = \frac{n_1^2}{\sqrt{n_1^2 - n_0^2 \sin^2 \alpha_0}}, \quad \text{for P polarized light} \quad (14)$$

where $\hat{n}_1$ is an effective refractive index, n_1 is material refractive index, n_0 is environment refractive index, α_1 is an angle of light propagation in material and α_0 is an angle of incidence.

Figure 66 shows the effective refractive indexes, calculated according to previous formulas. Here two environments – air (a)) and YAG crystal (b)) are selected as incident mediums. Different materials are showed, which can be deposited using conventional deposition methods, while effective refractive index below 1.45 can be achieved by using GLAD method.

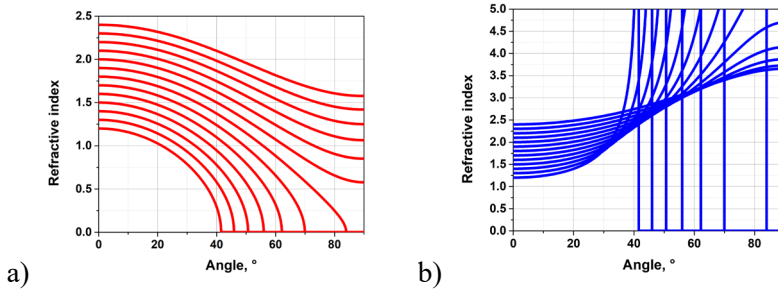


Figure 66. Dependency of effective refractive index on angle of incidence. (a) Incident material – air ($n_0=1$), (b) Incident material – YAG ($n_0=1.81$). Refractive indices correspond to IBS materials and YAG crystal: $n_{\text{SiO}_2}=1.47$, $n_{\text{Al}_2\text{O}_3}=1.65$, $n_{\text{YAG}}=1.81$, $n_{\text{HfO}_2}=2.02$, $n_{\text{Ta}_2\text{O}_5}=2.08$, $n_{\text{Nb}_2\text{O}_5}=2.21$; P polarization – blue lines, S polarization – red lines

4.1.2.1. Experimental method

A combination of two PVD methods is used – IBS and EBD, to deposit multilayer coatings. The final element was intended to be a YAG slab. However, in order to make experiments easier to analyze, we used YAG prisms. For the first part, two YAG prisms, together with fused silica (FS)

substrates were coated with 25 layers of nanostructured and dense silica (see Figure 67). These two coating designs: GLAD1 and GLAD2 are the same, but due to some errors during deposition process, final thicknesses were slightly different. Every second layer was deposited at 80° angle in terms of vapor flux to achieve low effective refractive index structures. Due to low effective refractive index, these coatings already experience TIR at a $42,5^\circ$ (S polarization) and a 42° (P polarization) angles of incidence (see Figure 68). In principle, minimal effective refractive index is used to achieve lowest angle at which TIR is visible. However, nanostructured layers, formed by GLAD technique has limitations in thickness. Due to competitive columnar growth, the inner nanostructure changes as well as effective refractive index throughout the layer. To avoid such inhomogeneities, every second layer is deposited at 0° angle of incidence [128].

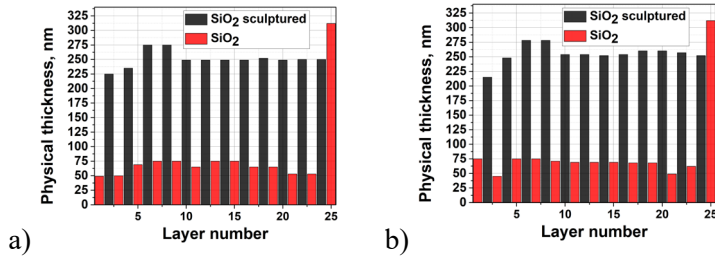


Figure 67. Theoretical designs of the GLAD coatings. GLAD1 theoretical design of $4.09 \mu\text{m}$ total thickness is presented in a) and GLAD2 theoretical design of $4.17 \mu\text{m}$ total thickness is presented in b)

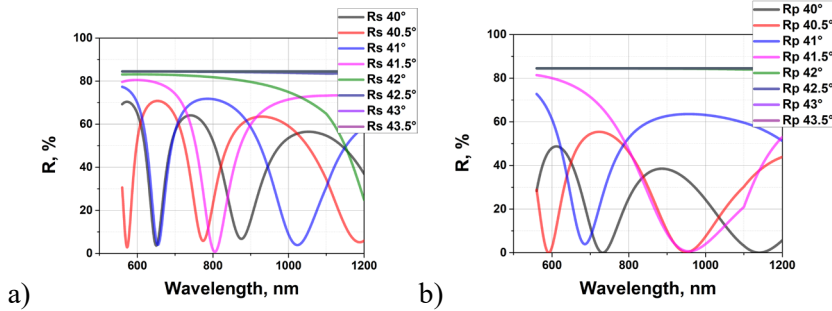


Figure 68. Theoretically modeled reflectance spectra of GLAD coating for a) S poliarization and b) P poliarization

During GLAD deposition process, additional FS substrates were also deposited with the same coating for spectral inspection (see Figure 69). Both samples were measured at 45° and compared with theoretical reflectance spectra. Some minor differences are visible between experimental and theoretical data. Nevertheless, in both cases reflectivity at the Bragg spectral

zone is similar. Minor errors and reduced spectral bandwidth indicate lower refractive index contrast than predicted in theoretical model. These discrepancies may have resulted from deposition thickness errors, lower refractive index value, inhomogeneity [129] and increased transmittance from nanoroughness [130].

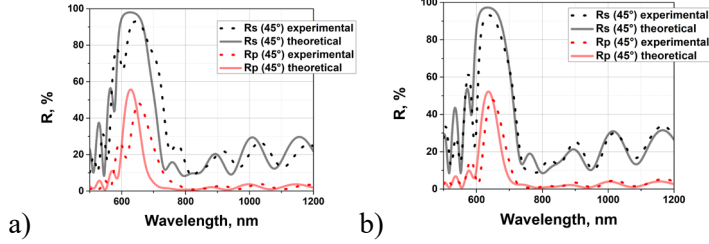


Figure 69. Theoretical reflectance spectra and measurements of a) GLAD1 and b) GLAD2 experimental samples

Multilayer GLAD films are coated with IBS and EBD technologies to fulfil other spectral characteristics described before. Final theoretical designs are presented in Figure 70. The final thicknesses of coatings are 5446 nm and 5830 nm for GLAD1 together with IBS part and GLAD2 with EBD part, respectively. As mentioned before, all these coatings were deposited on YAG prisms and FS substrates.

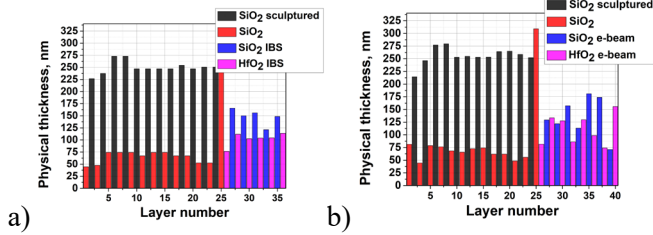


Figure 70. Theoretical designs of a) GLAD1+IBS and b) GLAD2+EBD

In order to estimate the spectral performance of the combined coatings, spectra measurements were performed for FS substrates for both polarizations at two angles of incidence: 13° and 45° . All data is plotted in Figure 71. Some spectral errors are visible when compared with theoretical data, even though IBS and EBD depositions were coated with great precision. Additional analyses are needed to evaluate the origin of errors in these coatings.

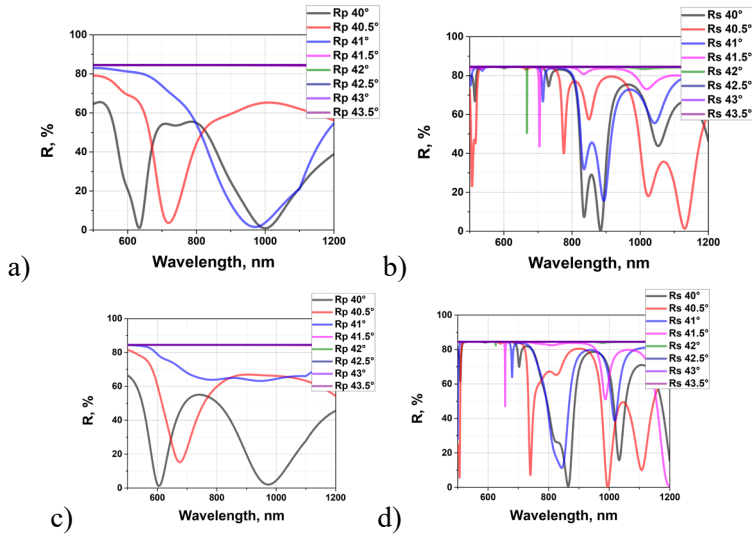
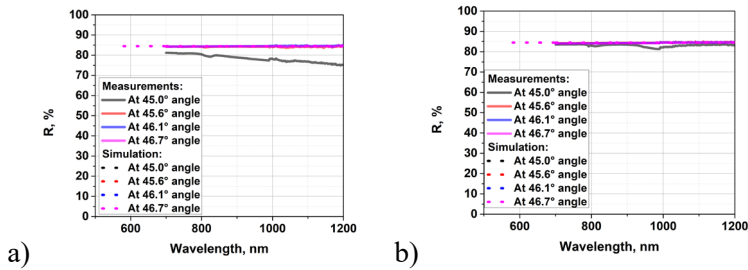


Figure 71. Internal reflectance of GLAD1+IBS coating from the substrate side for a) P and b) S polarizations and GLAD2+EBD coating from the substrate side for c) P and d) S polarizations

Theoretical internal reflectance spectra of both coatings GLAD1+IBS and GLAD2+EBD are presented in Figure 71 c) and d). Theoretically, additional coating on top of GLAD coatings shouldn't have any effect, meaning that TIR remains at the same angle above 42 degrees.

Using TIR configuration (see Figure 16) coated YAG prisms were measured in spectrometer at different angles. The obtained spectral performance of TIR is presented in Figure 72. In both cases, the achieved angle of TIR is at 46 degrees and above.



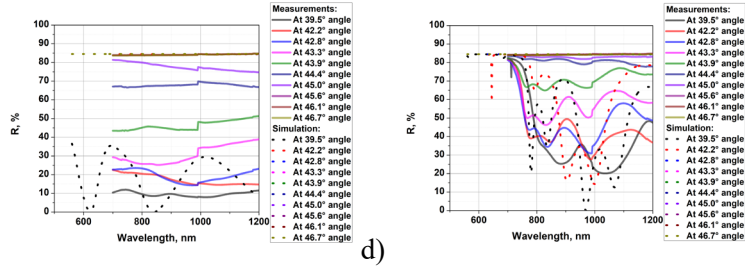


Figure 72. Spectrophotometric measurements of total internal reflectance using YAG prism for different angles of GLAD1+IBS experimental sample at a) P polarization and b) S polarization and GLAD2+EBD experimental sample at c) P polarization and d) S polarization

4.2.1.2. Analysis of experimental coatings

Hybrid coatings deposited on YAG crystal demonstrated TIR at 46 degrees and higher angles, however, theoretically minimum angle of TIR should be 42 degrees. Additional analysis was done in order to figure out the reason for discrepancy between theoretical and experimental results.

GLAD coatings, deposited on FS substrate were additionally tested using LIDT for 1064 nm wavelength setup at 45° AOI. GLAD1 and GLAD2 coatings LIDT values reached 52.6 J/cm² and 64.9 J/cm² respectively, indicating that coatings are applicable for high power laser systems. At 45° the coating is highly transparent at measured wavelength, but during TIR configuration most of laser beam energy will be reflected by porous silica coating. This shows high potential of GLAD coatings even in longer wavelengths using ns pulsed laser systems.

Both coatings were measured using SEM for structural analysis. It is worth mentioning, that GLAD1 together with IBS coating on Si wafer started to crack after several weeks in open air environment due to bad adhesion and some stress induced by IBS method (see Figure 73) [120]. It seems that columnar structure cannot withstand high stress values and peeled of the Si wafer substrate, although the same coating on FS and on YAG prism have no cracks due to adhesion. Undamaged cross-section areas of the coating were analyzed and the thickness was evaluated (see Figure 74). Theoretically GLAD1 coating thickness is 4.09 μm, which is similar with the thickness evaluated in SEM image (4.01 μm) without IBS coating. Such errors are expected when depositing GLAD coating as it is hard to precisely control nanostructured coatings using only quartz monitoring crystal. After analyzing

GLAD1 together with IBS coating, we can clearly see a change in thickness of nanostructured coating, which decreases to $3.69\ \mu\text{m}$ and the final thickness of the coating is $5.03\ \mu\text{m}$. GLAD coatings are highly porous, every 2nd layer is around 60 % porosity as showed in previous results (see Figure 20), while IBS coating is known to have high energies during deposition, which may induce this shrinking effect.

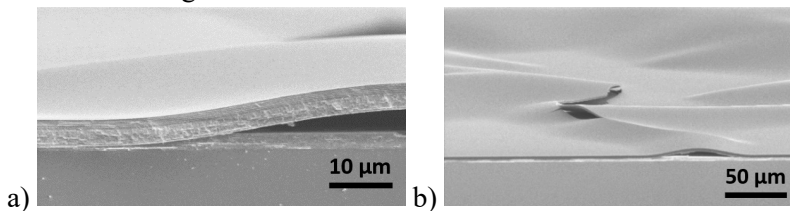


Figure 73. SEM images of GLAD1+IBS experimental sample cracking and delamination features

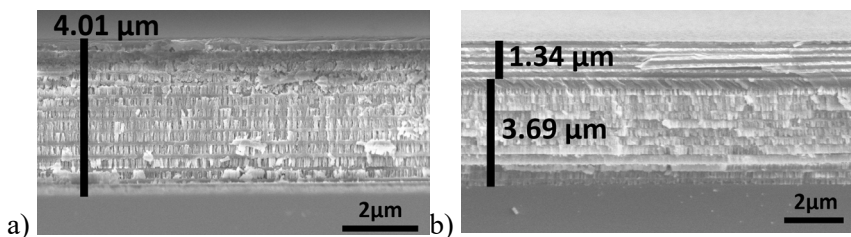


Figure 74. SEM images of a) only GLAD1 and b) GLAD1+IBS

Due to high energy of molecules and atoms during IBS deposition, they may transfer part of kinetic energy to the surface of porous GLAD coating resulting in a decrease of thickness and increase of effective refractive index of silica layers. We can see some spectral differences in reflectance measurements, which may be induced by shrinking of nanostructured coatings. This will also have an effect to the TIR effect, where minimum effective refractive index is needed. Using IBS technology to deposit on porous all-silica coatings for enhancement of spectral properties may not be so effective.

Same structural analyzes were performed for the GLAD2 together with EBD coatings. Vapor flux during EBD method has significantly lower energies, therefore much lower pressure is applied to GLAD coating. In this case, no cracks were found on the Si wafer, indicating lower stress of the coating. SEM images showed that GLAD2 coating is around $3.96\ \mu\text{m}$ (see Figure 75) and after EBD deposition, the coating thickness was suppressed to $3.85\ \mu\text{m}$, while the total thickness of coating is $5.69\ \mu\text{m}$. Theoretically, GLAD coating should be $4.17\ \mu\text{m}$ and the total thickness of GLAD1 together with

EBD around 6 μm . Total physical thicknesses of the coatings were also confirmed by profilometer measurements (see Figure 76).

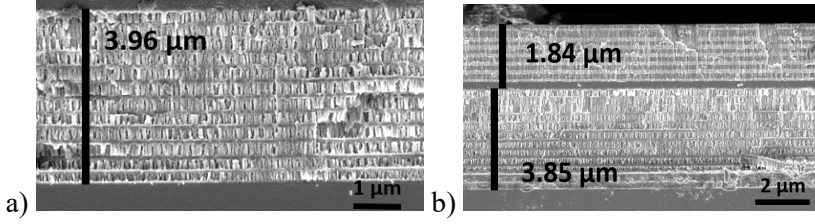


Figure 75. SEM images of a) only GLAD2, b) GLAD2+EBD

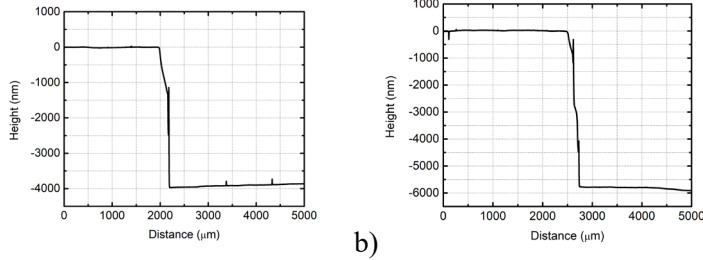


Figure 76. Profilometer measurements of a) GLAD coating (thickness is 3968 nm) and b) GLAD + EBD deposition (thickness 5767 nm)

The suppression of GLAD coatings after external pressure is applied was already known [131]. We can calculate the thickness reduction of porous layers using formulas described in previously cited work. GLAD coating thickness is selected to be 3000 nm, porosity of sculptured layers is 60 %. The reduction of thickness for IBS coated thin films was calculated as ~ 970 nm and for EBD coated samples ~ 180 nm. Experimentally we demonstrated three times and two times lower reduction respectively. However, during experiment we used dense silica interlayers between every ~ 250 nm porous silica in order to strengthen the physical properties of the coating. The interlayers were deposited at 0° AOI, meaning that some material may reach the gaps between the porous silica columns, which also increase the density of the film.

4.2.1.3. Measurement of spectral parameters of coated YAG prism

After structural analysis, coated FS substrates were measured using standard configuration (see Figure 16) for both polarizations at 13° and 45° angles (see Figure 77). From spectrometer measurements we can see that there are some errors visible, even though IBS and EBD coatings were deposited with great precision. These errors appeared because of the GLAD nanostructured coating, which refractive index and thickness changed.

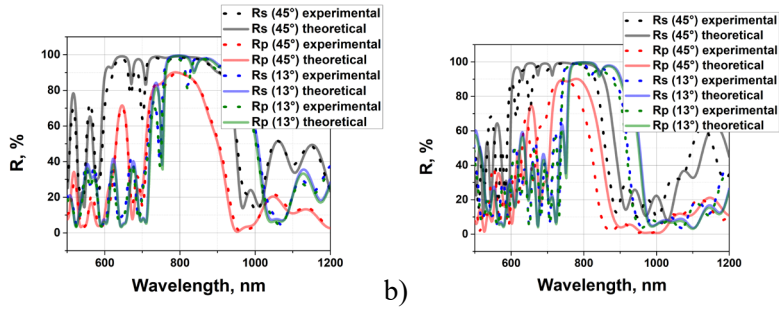


Figure 77. Calculated (theoretical) and measured (experimental) spectral parameters of combined coatings of a) GLAD1+IBS and b) GLAD2+EBD

Measured spectra of coated YAG crystals were analyzed deeper with some reverse engineering design which are provided in Figure 79. After initial measurement was compared to unmodified theoretical simulation, large mismatch was found. Additional structural analysis revealed that GLAD coating structures were modified during IBS and EBD formation, therefore we need to simulate what are the actual changes of nanostructured layers. Two major observations have to be encountered: TIR conditions were not met for angles below 46° and many errors visible between experimental and theoretical spectra (see Figure 78). We must take into account, that the cone angle of the measurements, possibly smoothens the resulting spectral dependence, therefore, to fit calculated spectra conical light source beam instead of plane wave uniform front must be estimated.

Conical light source was included ($\pm 1^\circ$ uniform distribution conical beam) and we can see major improvements as the spectra's fit more accurately (see Figure 79). However, there are still some mismatching between experimental and theoretical spectra. Finally, we had to increase the refractive index of nanostructured layers by 6 % in order to have a better fit. As we can see from plotted data, TIR of coated YAG crystal is achieved at 46° and higher angles because the effective refractive index, which was initially expected, increased of nanostructured layers (see Figure 80). This might have happened because of the suppression during IBS or EBD depositions or the coating absorbed water from the air environment increasing the effective refractive index of porous silica layers.

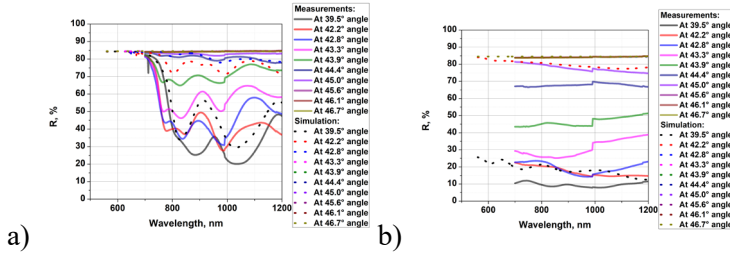


Figure 78. Measurements and calculated reflectance spectra of GLAD2+EBD on YAG prism a) P polarization and b) S polarization. In theoretical model convergence of the beam is included

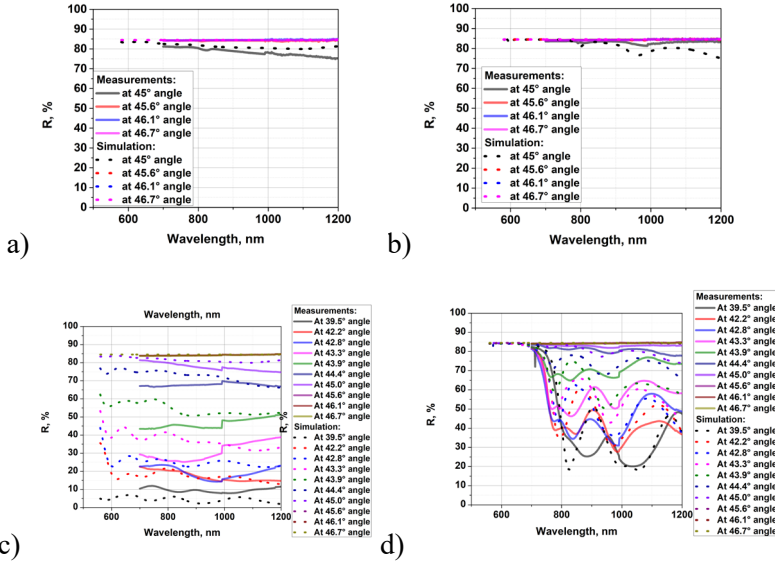


Figure 79. Measurements and calculated reflectance spectra of GLAD1+IBS on YAG prism a) P polarization and b) S polarization and GLAD2+EBD on YAG prism c) P polarization and d) S polarization. In theoretical model convergence of the beam is included and refractive index is increased by 6 %

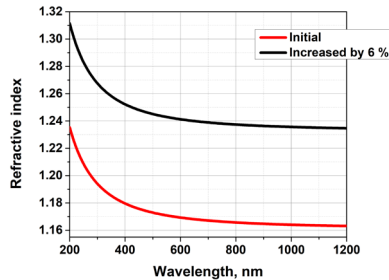


Figure 80. Refractive indices of GLAD porous layers

To test how water absorption affects refractive index of porous silica layers, hybrid coatings deposited on FS substrates were annealed up to 200° C. Transmittance spectra were measured of coating immediately after annealing, then after several hours, 1 day and 2 days. All spectral measurements are plotted in Figure 81. Experiment revealed, that refractive index of porous layers changes from initial value by 3 % in one to two days and stays the same. After several hours, the refractive index increases by 1 %. GLAD coatings refractive index changes by total of 3 % by absorbing water from the environment, however, from coated YAG prism measurements we see a change of 6 % of refractive index, meaning that the rest 3 % changed due to suppression of nanostructured layers.

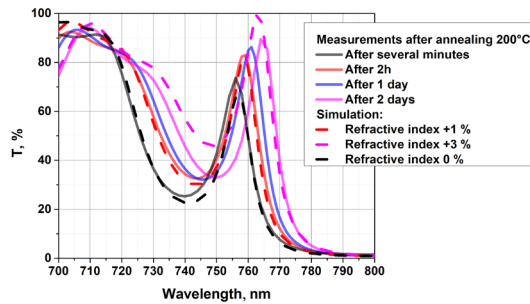


Figure 81. Measurements and modeled transmittance spectra of GLAD1+IBS after annealing coatings up to 200° C

4.2.1.4. The main results and conclusions

Nanostructured multilayer silica coatings were coated on YAG zigzag slab lasers for improving TIR effect. A combination of GLAD coatings with ion beam sputtered and standard EBD additional multilayers allowed to reach total internal reflection effect in YAG prism at 45.5 degrees and higher angles. The TIR angle was limited by increased refractive index in nanostructured silica due to induced internal stress of dense layers coated by IBS and EBD technologies. Proposed porous layer structure for zigzag slab laser setup is a novel approach, which enhances the range of total internal reflection angles and due to multilayer structure allows to gain necessary spectral performance at other angles.

5. MAIN RESULTS AND CONCLUSIONS OF THE THESIS

1. Single-layer coatings of different materials (Nb_2O_5 , Al_2O_3 , Ta_2O_5 and SiO_2) were evaporated at various angle (0° , 50° , 60° , 70° and 80°) using the GLAD method. The porosity of these coatings increased with the deposition angle due to shadowing effects, as confirmed by Bruggeman Effective Media Theory and SEM imaging. LIDT varied significantly among materials: SiO_2 achieved the highest values ($>100 \text{ J/cm}^2$ at low deposition angles). Al_2O_3 demonstrated consistent resistance ($\sim 32.29 \text{ J/cm}^2$) regardless of porosity. Nb_2O_5 and Ta_2O_5 showed lower resistivity, with porosity playing a minor role. The defects, created during deposition process had the highest influence, which affected the LIDT values of single-layer coatings.
2. All-silica multilayer coatings were developed using GLAD with a combination of dense and porous SiO_2 layers. Porous layers absorbed water and other environmental particles, leading to spectral shifts and decreased LIDT. Initial 1-on-1 LIDT values of all-silica mirrors reached $\sim 80 \text{ J/cm}^2$ but degraded to $\sim 16 \text{ J/cm}^2$ after three weeks of exposure to ambient air. Storing mirrors in desiccators or gas-filled environments (e.g., argon, nitrogen) significantly improved LIDT, reaching values up to 100 J/cm^2 in certain cases. Heat treatment ($\sim 200^\circ\text{C}$) partially restored LIDT by reducing water content, and ammonia treatments induced chemical condensation in silica layers, improving bonding but not eliminating instability.
3. LLIA enabled gradual energy ramping, increasing LIDT up to $180\text{--}200 \text{ J/cm}^2$ in conditioned samples. The conditioning process appeared to "clear" defects, enhancing the resilience of porous coatings. LLIA in inert gas environments yielded better results than in air. However, heating during LLIA reduced LIDT due to stress-related cracks, suggesting temperature's detrimental effect on stability. SEM and Nomarski imaging revealed damage morphologies linked to stress and particle absorption. Porous structures exhibited resilience to thermal expansion but were vulnerable to humidity and stress-induced cracks. Storing coatings in controlled environments (e.g., argon or nitrogen) and using LLIA protocols with slow energy ramping (0.125 J/cm^2 increment per pulse) showed the most promise for maintaining optical performance over time.
4. Hybrid multilayer coatings combining IBS and GLAD techniques were developed to improve LIDT. Enhanced resistivity was demonstrated, with LIDT values reaching up to 47 J/cm^2 for hybrid all-silica mirrors after LLIA. This technique effectively combined low-scattering, high-resistivity layers.
5. All-silica coatings were tested for femtosecond laser systems and achieved higher LIDT values than traditional IBS coatings. However, unexpected

fatigue effects and structural vulnerabilities were observed under certain conditions, particularly for nanostructured porous silica layers.

6. Nanostructured all-silica coatings were applied to YAG crystals, achieving high LIDT values of 222 J/cm² for unetched crystals and up to 140 J/cm² for plasma-etched crystals using LLIA. Plasma-etched surfaces exhibited more defects, reducing LIDT performance.

7. GLAD coatings were used to optimize TIR configurations in YAG crystals, achieving effective reflection angles as low as 46°. However, discrepancies between theoretical and experimental results highlighted challenges such as nanostructural suppression and environmental water absorption. SEM revealed that GLAD coatings experienced thickness reduction and increased refractive indices when overcoated using IBS or EBD processes. Water absorption by porous silica layers contributed to refractive index changes of up to 3%, affecting spectral performance.

RECOMMENDATIONS

This work investigates the GLAD method, primarily using all-silica material for the formation of various optical elements. Although these coatings degrade over time when exposed to open-air environment, they can perform well under stable conditions, particularly with controlled humidity. However, in environment where conditions fluctuate, the coatings degrade. In such cases, local laser radiation annealing can be employed to enhance the optical performance of all-silica nanostructured coatings.

Elements such as HR, AR, or other coatings produced using GLAD method are highly suitable for high-power laser systems in vacuum conditions, where humidity is minimal. Nanostructured coatings demonstrate significant potential when used as upgrades by depositing multilayer stacks on existing optical components, thereby increasing LIDT of these elements. Future research will focus on forming nanostructured coatings by combining various materials, such as titania and porous silica, to maximize the refractive index difference and create the widest possible Bragg mirrors for the visible or near-infrared range. These coatings could have unique applications in multi-pass cells for spectral broadening and laser pulse compression down to around 15 fs.

For nanostructured coatings to be applicable in everyday life, future research is needed to understand how these sculptured coatings behave under varying humidity levels. Initial observations indicate that even low-stress porous coatings experience an increase in stress when environmental conditions change. Therefore, it is crucial to monitor stress levels as environmental conditions, including humidity and temperature, fluctuate.

SANTRAUKA

Santrumpų sąrašas

PVD	Fizinis garų nusodinimas, Physical Vapor Deposition
EBD	Garinimas elektronų pluoštu, Electron Beam Deposition
GLAD	Nusodinimas slystančiu kampu, Glancing Angle Deposition
AFM	Atominių jėgų mikroskopas, Atomic Force Microscopy
SEM	Skenuojantis elektronų mikroskopas, Scanning Electron Microscopy
LIDT	Lazerio indukuotos pažaidos slenkstis, Laser-induced Damage Threshold
LID	Lazerio sukulto užlinkimo metodas, Laser-induced deflection
FS	Lydytas kvarcas, Fused Silica
AR	Skaidinantri danga, Anti-reflective
HR	Didelio atspindžio danga, High-reflective
QWOT	Ketvirtis optinio bangos ilgio storis, Quarter Wavelength Optical Thickness
LLIA	Lokalus lazerio spinduliuotės atkaitinimas, Local laser irradiation annealing
AOI	Kritimo kampas, Angle of incidence

Ivadas

Lazerinės eros pradžia laikoma 1960 m. gegužės 16 d. [1], kai Theodore'as Maimanas pademonstravo pirmąjį lazerį. Jo eksperimentinę sąranką sudarė rubino strypas, kurio paviršiai buvo padengti sidabru, o didelės galios blyksčių lempa sukėlė lazerinę spinduliuotę. Netrukus po to Paulas D. Makeris ir jo kolegos [2] savo novatoriškame darbe užfiksavo pirmąjį lazerio sukeltos pažaidos atvejį dielektrinėse plėvelėse. Šis atradimas atvėrė naują tyrimų sritį, skirtą optinių dangų kūrimui ir optimizavimui.

Lazerinių sistemų vystymasis paskatino ir pažangių optinių dangų poreikį. Atsirado tokios technologijos, kaip fizinė garų nusodinimo (PVD) [3] ir cheminė garų nusodinimo (CVD) [4] metodikos, leidžiančios kurti vis sudėtingesnius ir tikslesnius optinius elementus. Nuolat didėjantis lazerių intensyvumas bei trumpėjanti impulsų trukmė skatino kurti geresnių savybių ir didesnio patikimumo dangas. Lazerinių sistemų evoliucija darė didelę įtaką įvairioms mokslinių tyrimų sritims: telekomunikacijoms, medicinai, aukštųjų technologijų pramonei ir kitoms.

Nepaisant reikšmingos pažangos, lazerinėse sistemose optiniai elementai – tokie kaip antirefleksinės (AR) dangos, veidrodžiai, poliarizatoriai ir kt. – vis dar riboja tolesnį technologinį tobulėjimą. Šiuolaikiniai nusodinimo metodai leidžia gaminti optinius elementus su išskirtiniu sub-nanometrinio storio tikslumu, maža sugertimi ir stabiliais lūžio rodikliais [5], [6]. Standartinė konfigūracija, naudojanti pakaitomis išdėstytas aukšto ir žemo lūžio rodiklio medžiagas, suteikia reikiamas optines savybes. Tačiau aukšto lūžio rodiklio medžiagos dažniausiai turi mažesnę draustinės juostos energiją, o tai mažina jų atsparumą lazerio spinduliuotei [7]. Siekiant, kad lazerinės sistemos taptų labiau pritaikomos kasdieniam naudojimui ir kad jų matmenys būtų mažesni, reikia inovatyvaus požiūrio – esamus optinius komponentus būtina pakeisti kompaktiškesniais. Vienas iš unikaliausių sprendimų yra daugiasluoksnių dangų formavimas tiesiogiai ant esamų mikrolazerių sistemų elementų (nelinijinių kristalų).

Vienas perspektyviausių būdų šiems iššūkiams spręsti yra garinimo slystančiu kampu (GLAD) metodas [8]. Reguluojant pagrindo posvyrio kampą garų srauto atžvilgiu nusodinimo metu, GLAD leidžia kontroliuoti medžiagų efektyvų lūžio rodiklį. Tai suteikia galimybę kurti daugiasluoksnes struktūras naudojant tik vieną medžiagą, o lūžio rodiklių kontrastas pasiekiamas manipuliuojant pagrindo padėtimi nusodinimo metu. Tokia technologija leidžia gaminti AR dangas, aukšto atspindžio (HR) veidrodžius bei kitus optinius elementus [8], [9]. Be to, standartinių ir nanostruktūrinių

sluoksnių derinimas gali dar labiau pagerinti esamų komponentų optines savybes, todėl jie tampa tinkamesni modernioms lazerinėms sistemoms [10].

Galimybė modifikuoti dangų vidinę struktūrą ir efektyvius lūžio rodiklius atveria naujas technologines galimybes optinių elementų kūrimui. Vienas iš reikšmingų pritaikymų – nanostruktūrinių dangų naudojimas siekiant sustiprinti visiško vidinio atspindžio (TIR) reiškinių YAG kristaluose, kurie yra svarbūs zigzaginės ertmės architektūrose plokštelinėse lazerinėse sistemose. Tokios pažangios dangos išplečia TIR taikymo ribas, užtikrindamos patikimesnį ir efektyvesnį lazerinių sistemų veikimą. Tačiau norint pasiekti stabilų našumą, būtina spręsti tokius iššūkius kaip lūžio rodiklio nestabilumas ir aplinkos poveikis – drėgmės ar kenksmingų dalelių absorbcijos sukeltas degradavimas.

Šioje disertacijoje nagrinėjamas nanostruktūrinių dangų projektavimas, gamyba ir charakterizavimas, daugiausia dėmesio skiriant jų optinėms savybėms ir ilgaamžiškumui. Visų pirma, analizuojamos įvairios medžiagos, siekiant nustatyti jų tinkamumą aukštos kokybės dangoms. Antra, tiriami visos silicio dioksido veidrodžių gamybos metodai bei jų degradacijos prevencijos strategijos, įskaitant aplinkos stabilizavimą ir atkaitinimą. Trečia, nanostruktūrinės dangos yra tiesiogiai nusodinamos ant YAG kristalų ir tiriamos. Kuriami unikalūs dizainai, siekiant išprovokuoti TIR reiškinių, taip įrodant šių dangų pritaikomumą zigzaginės ertmės architektūrose plokštelinėse lazerinėse sistemose. Sprendžiant nanostruktūrinių dangų technologinius ir aplinkosauginius iššūkius, šiame darbe siekiama prisidėti prie patvaresnių ir efektyvesnių optinių elementų kūrimo naujos kartos lazerinėms sistemoms.

Disertacijos tikslas

Nanostruktūrinių sluoksnių optinio stabilumo tyrimas ir skulptūrinių plonų sluoksnių taikymo srities išplėtimas gaminant optinius elementus tiesiogiai ant YAG lazerinių kristalų.

Disertacijos moksliniai uždaviniai

1. Ištirti nusodinimo kampų įtaką skirtingų medžiagų porėtumui ir lūžio rodikliams bei nustatyti koreliaciją tarp porėtumo ir lazerio sukeltos pažaidos slenksčio.
2. Ištirti silicio dioksido (SiO_2) daugiasluoksnių dangų formavimąsi ir stabilumą.
3. Analizuoti aplinkos veiksnių poveikį silicio dioksido veidrodžių optinėms savybėms ir ištestuoti skirtingus metodus siekiant pagerinti veidrodžių optinį našumą bei patvarumą.

4. Tiesiogiai nusodinti silicio dioksido dangas ant lazerinių kristalų ir analizuoti jų optinį našumą bei stabilumą aplinkoje.
5. Sukurti daugiasluoksnės dangos nusodinimo metodą ant YAG kristalo, siekiant indukuoti visiško vidinio atspindžio (TIR) reiškinių.

Mokslinis naujumas ir praktinė vertė

Nanostruktūrinės dangos yra detalios ištirtos ir turi didelį potencialą optinių elementų formavimui. Šioje disertacijoje išsamiai analizuojama skirtingų vidinių struktūrų medžiagų gamyba. Pagrindinis šio darbo tikslas – atverti naujas galimybes taikant skulptūrinės dangas ant lazerinių kristalų, siekiant pagerinti esamas lazerines sistemas. Disertacijos mokslinis naujumas ir praktinė reikšmė gali būti apibendrinta šiais teiginiais:

- Šis tyrimas yra pirmasis išsamus lazerio sukeltos pažaidos slenksčio tyrimas, taikant garinimo slystančiu kampu metodą skirtingoms medžiagoms (Nb_2O_5 , Al_2O_3 , Ta_2O_5 and SiO_2). Gauti rezultatai sudaro pagrindą tolimesniems porėtų optinių dangų pažeidimo mechanizmų tyrimams.
- Silicio oksido (SiO_2) veidrodžiai buvo tiriami skirtingose aplinkose, siekiant išvengti degradacijos poveikio. Nors silicio oksido veidrodžiai iš pradžių yra jautrūs aplinkos sąlygoms, strateginiai metodai gali efektyviai stabilizuoti jų optines savybes. Perspektyviausia aplinka, siekiant išvengti degradacijos, buvo azoto arba argono dujų aplinka.
- Silicio oksido veidrodžiams pritaikytas lokalus lazerio spinduliuotės atkaitinimas. Taikant šį metodą, buvo gautos labai aukštos LIDT vertės, rodančios, kad silicio oksido veidrodžiai gali atlaikyti itin didelę lazerio spinduliuotės energiją (180 J/cm^2 esant 355 nm bangos ilgiui nanosekundžių režime). Dėl šio atradimo, tokios dangos yra perspektyvus sprendimas didelės galios lazerinėms sistemoms.
- Ant YAG kristalo buvo suformuotos ir ištirtos nanostruktūrinės SiO_2 dangos. Nusodintos Brego veidrodžio dangos ties 532 nm bangos ilgiu pasižymi aukštu lazerio sukeltos pažaidos slenksčiu ($>140 \text{ J/cm}^2$) nanosekundžių režimo impulsiniame lazeryje.
- Šiame darbe pateiktas tyrimas parodo naują metodą, leidžiantį pagerinti YAG kristalų veikimą lazerinėje sistemoje, naudojant nanostruktūrinės dangas. Taikomi GLAD metodai rodo potencialą išplėsti visiško vidaus atspindžio kampinį diapazoną nuo 55° iki

46° YAG prizmėse, taikant unikalius SiO₂ nanostruktūrinius skulptūrinius sluoksnius.

Ginamieji teiginiai

1. Nanostruktūrizuotų Nb₂O₅, Al₂O₃, Ta₂O₅ ir SiO₂ dangų, nusodintų taikant GLAD metodą, LIDT reikšmėms daugiau įtakos turi defektai, o ne dangų porėtumas.
2. Daugiasluoksnių silicio oksido veidrodžių optinių savybių pablogėjimą galima sumažinti laikant juos azoto arba argono aplinkoje, o ne atvira ore.
3. Taikant lokalsios lazerio spinduliuotės atkaitinimo metodą su ne didesniu kaip 0.125 J/cm² didinimu vienam impulsui, silicio oksido veidrodžiai gali atlaikyti labai aukštas energijas iki 180 J/cm², naudojant nanosekundžių impulsų režimą, 355 nm bangos ilgiui.
4. Nanostruktūrizuoto SiO₂ nusodinimas tarp YAG kristalų ir tankios daugiasluoksnės dangos leidžia išplėsti TIR kampinį diapazoną YAG kristaluose iki 46 laipsnių dėl mažesnio efektyvaus lūžio rodiklio.

Aprobacija

Mokslinės publikacijos, tiesiogiai susijusios su disertacijos tema (žurnaluose, referuojamuose CA WoS duomenų bazėje):

1. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Near fundamental nanosecond laser damage resistance of nanostructured all-silica mirrors at 355 nm by local laser irradiation”, Results in Optics, 14, 100616, 2024

2. **L. Ramalis**, S. Melnikas, D. Buinovskis, T. Tolenis “Enhancement of total internal reflection in Nd:YAG crystals by multilayer nanostructured coatings”, Optics and Laser Technology, 2025

Mokslinės publikacijos tiesiogiai susijusios su disertacijos tema (konferencijų publikacijos)

1. **L. Ramalis**, L. Grinevičiūtė, R. Buzelis, T. Tolenis “Formation of all-silica sculptured thin films based optical elements on crystal substrates”, Proc. SPIE 11467, Nanoengineering: Fabrication, Properties, Optics, Thin Films, and Devices XVII, 114671V, <https://doi.org/10.1117/12.2568598>, 2020

2. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, Proc. SPIE 11872, Advances in Optical Thin Films VII, 1187210 2021

3. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, Proc. SPIE 11910, Laser-Induced Damage in Optical Materials, 1191016, <https://doi.org/10.1117/12.2598667>, 2021

4. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, Proc. SPIE 12202, Nanoengineering: Fabrication, Properties, Optics, Thin Films, and Devices XIX, 1220206, <https://doi.org/10.1117/12.2633935>, 2022

5. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, Proc. SPIE 12300, Laser-Induced Damage in Optical Materials 2022, 123000O, <https://doi.org/10.1117/12.2641172>, 2022

Kitos mokslinės publikacijos (žurnaluose, referuojamuose CA WoS duomenų bazėje):

1. L. Grinevičiūtė, **L. Ramalis**, R. Buzelis, T. Tolenis “Highly resistant all-silica polarizing coatings for normal incidence applications”, Optics letters, Vol. 46, No. 4, 2021

2. S. Melnikas, **L. Ramalis**, S. Kičas, T. Tolenis “Broadband chirped mirrors with a porous top layer for smooth group delay dispersion”, Appl. Opt. 60, 8181-8187, 2021

Konferencijos, tiesiogiai susijusios su disertacijos tema:

1. **L. Ramalis**, L. Grinevičiūtė, R. Buzelis, T. Tolenis “Formation of all-silica sculptured thin films based optical elements on crystal substrates”, SPIE. Nanoscience + Engineering, 24-28 August 2020, Oral-Online pr.

2. **L. Ramalis**, L. Grinevičiūtė, R. Buzelis, T. Tolenis “Anisotropic Thin Films Based Polarizing Coatings For High Power Lasers”, Advanced materials and technologies 2020, Palanga, Lithuania, 24-28 August 2020, poster pr.

3. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, Surfaces, Interfaces and Coatings Technologies International conference, Paris, France, 07-09 April 2011, Oral-Online pr.

4. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, SPIE. Optical Design Systems, Digital Forum, 13-17 September 2021, Oral pr.

5. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Skulptūrinių plonų sluoksnių pagrindu suformuoti silicio oksido veidrodžiai didelės galios lazeriams”, Lietuvos Nacionalinė Fizikų Konferencija. Vilnius, Lithuania, 6-8 October 2021, poster pr.

6. **L. Ramalis**, U. Norkutė, R. Buzelis, L. Grinevičiūtė, T. Tolenis “Sculptured thin film based all-silica mirrors for high power lasers”, SPIE. Laser Damage, 12-15 October 2021, Oral-Online pr.

7. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, SPIE Nanoscience + Engineering, San Diego, US, 21-26 August 2022, Oral pr.

8. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, Optical Interference Coatings, Whistler, Canada, 17 June 2022, poster pr.

9. **L. Ramalis**, R. Buzelis, G. Dolmantaitė, T. Tolenis “Laser conditioning of all-silica mirrors”, SPIE Laser Damage, Rochester, US, 18-22 September 2022, poster pr.

10. **L. Ramalis**, A. Strazdas, T. Tolenis “Broad band mirrors using nanostructured thin films”, SPIE. Optical Design Systems, April 7-11 2024, poster pr.

Autoriaus asmeninis ir bendraautorių indėlis

Disertacijos autoriaus ir pagrindinių bendraautorių indėlis aprašytas šiame tekste:

Autorius asmeniškai suplanavo arba aktyviai dalyvavo planuojant visus eksperimentus. Taip pat atliko arba prižiūrėjo visus eksperimentinius plonų sluoksnių nusodinimo procesus, vykdė spektrofotometrinius matavimus ir lazerio sukeltos pažaidos slenksčio (LIDT) matavimus. Visą nanostruktūrinių sluoksnių analizę atliko autorius.

Dr. T. Tolenis prižiūrėjo nusodinimo procesus, dalyvavo visų eksperimentų planavime.

Dr. R. Buzelis dalyvavo visuose LIDT matavimuose.

Dr. G. Abromavičius ėsdino lydyto kvarco (fused silica) pagrindus, naudotus visų vienasluoksnių dangų nusodinimui.

Dr. A. Selskis atliko SEM matavimus.

Dr. S. Melnikas atliko IBS nusodinimo procesus, dalyvavo TIR dangų projektavime ir charakterizavime.

P. Sebastianas Paschelis atliko LIDT matavimus „Laser Zentrum Hannover“ laboratorijoje, naudojant skirtingas aplinkas.

Visi bendra autoriai dalyvavo rengiant mokslines publikacijas.

Literatūros apžvalga

Pirmajame disertacijos skyriuje pateikta literatūros apžvalga. Aprašomi elementai, kurių savybės analizuojamos disertacijoje – skaidrinančios dangos, Brego veidrodžiai, visiško vidaus atspindžio elementai. Taip pat šiame poskyryje aprašomi keli skaidrinančių dangų taikymai ant lazerinių kristalų. Kitame poskyryje aptariamas dielektrinių dangų optinis atsparumas ir pagrindiniai metodai, skirti didinti optinių dangų atsparumą. Paskutiniame poskyryje supažindinama su pagrindiniais optinių dangų nusodinimo metodais, kurie naudojami disertacijoje. Detalai aprašomas dangų nusodinimas naudojant garinimo kampu metodiką, kai yra formuojami nanostruktūrizuoti sluoksniai.

Eksperimentinės metodikos

Antrame disertacijos skyriuje pateikiami visi matavimo metodų aprašymai, kurie buvo naudojami vykdant eksperimentus. Skyrius sudarytas iš trijų dalių: optiniai matavimai, struktūriniai matavimai ir bandinių paruošimas. Pirmajame poskyryje aprašomas spektrofotometras, baltos šviesos interferometras, lazerio sukulto užlinkimo metodas ir lazerio indukuotos pažaidos slenksčio matavimo metodas. Antrajame poskyryje aprašomas skenuojantis elektronų mikroskopas, atominių jėgų mikroskopas ir Ramano sklaidos spektroskopijos metodas, kurie yra skirti dangų struktūrinėms savybėms analizuoti. Paskutiniame poskyryje aprašomi paruošiamieji darbai prieš kiekvieną garinimo procesą, norint gauti aukštos kokybės dangas.

Rezultatai

Rezultatai yra suskirstyti į du skyrius: pirmajame skyriuje yra pristatomi darbai, susiję su skulptūrinių dangų detalioja analize ant įprastų lydyto kvarco stikliukų, antrajame skyriuje analizuojamos skulptūrinės dangos, kurios yra nusodinamos ant lazerinių kristalinių padėklų.

Vienasluoksnių dangų analizė

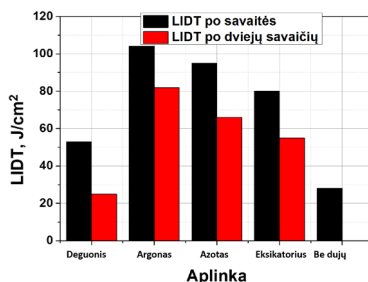
Pirmaisiais metais buvo atliktas vienasluoksnių dangų nusodinimas naudojant garinimo kampu technologiją skirtingais kampais (0° , 50° , 60° , 70° ir 80°). Pasirinktos skirtingos medžiagos (Nb_2O_5 , Al_2O_3 , Ta_2O_5 ir SiO_2), kurios plačiai naudojamos optinių elementų formavimui siekiant išsiaiškinti, kokią įtaką dangų porėtumas turi lazeriniam atsparumui. Darbe pademonstruota,

kaip skirtingoms medžiagoms galioja šešėliavimo efektas ir kinta dangų optinės bei struktūrinės savybės. Nepaisant to, kad didesnis porėtumas teoriškai gali padėti sumažinti šiluminius įtempius, tankios dangos pasižymėjo didesniu atsparumu lazerinei spinduliutei. Defektai, susidarantys dengimo proceso metu, turėjo didžiausią įtaką, o tai ir paveikė vienasluoksnių dangų lazerinio atsparumo vertes. Tolimesniems eksperimentams buvo pasirinkta SiO_2 , kaip atspariausia lazerinei spinduliutei medžiaga, iš kurios formuojamos daugiasluoksnės dangos.

Silicio oksido veidrodžių analizė

Šiame skyriuje pristatomas Brego veidrodžio formavimas naudojant vieną medžiagą – silicio oksidą - siekiant gauti didelio atsparumo lazerinei spinduliutei optinius elementus. Taikant garinimo kampu metodą, formuojamas Brego veidrodis, kur žemo lūžio rodiklio medžiaga yra formuojama pakreipus bandinį 70° kampu garų srauto atžvilgiu, o aukšto lūžio rodiklio medžiaga gaunama garinant 0° kampu. Dėl struktūriškai suformuoto lūžio rodiklių skirtumo gaunamas Brego veidrodis specifiniam bangos ilgiui (šiuo atveju 355 nm bangos ilgiui).

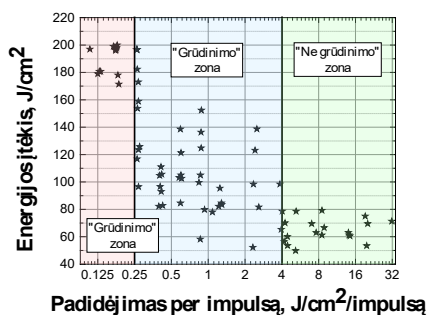
Dėl didelio porėtumo optiniai elementai yra linkę sugerti aplinkoje esančias daleles, įskaitant vandenį, todėl, laikui bėgant, tokios dangos degraduoja. Šiame skyriuje atliekama serija eksperimentų siekiant apžvelgti degradacijos požymius: spektrinį poslinkį ir atsparumą lazerinei spinduliutei. Siekiant išvengti degradacijos, bandiniai yra patalpinami į skirtingų garų terpes (deguonies, argono ir azoto), taip pat į eksikatorių ir lyginami rezultatai su ore patalpintais bandiniais. Gauti rezultatai parodė, jog argono ir azoto dujos labiausiai sulaukė dangų degradacijos efektą, tačiau visiškai išvengti to nepavyko (žiūrėti 1 pav.). Tolimesni eksperimentai vykdomi siekiant išvengti degradacijos nanostruktūrizuotose dangose.



1 pav. Lazerio indukuotos pažaidos slenksčio rezultatų histograma, kai bandiniai patalpinti į skirtingas aplinkas

Kitame etape lokalus lazerio spinduliuotės atkaitinimas (LLIA) yra testuojamas silicio oksido Brego veidrodžiams. Šio metodo metu lazerio energija yra pamažu keliama atitinkamu greičiu, pradinei energijai esant 10 J/cm^2 , siekiant pagerinti nanostruktūrizuotų veidrodžių optinį atsparumą. Po pirmų eksperimentų pastebėta, kad Brego veidrodžiai gali atlaikyti iki 180 J/cm^2 be jokių pažeidimų, tuo tarpu LIDT taikant 1-on-1 metodą siekia apie 14.7 J/cm^2 .

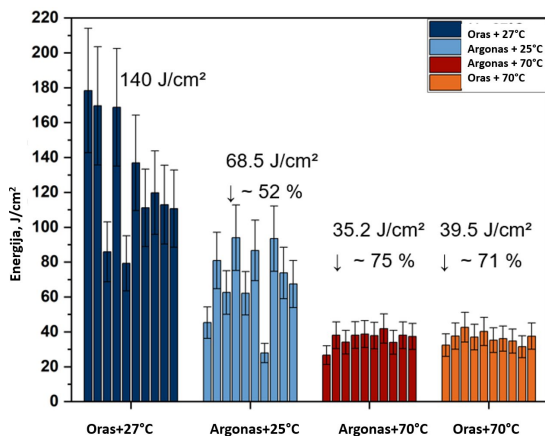
Taikomi skirtingi protokolai, keičiant lazerio impulso energijos kėlimo greitį (žiūrėti 2 pav.) norint detaliau ištirti šį metodą. Pagal lazerio impulso energijos kilimo greitį gaunamos trys skirtingos zonos: pirmoji zona, kur nevyksta grūdinimo efektas (nuo 32 iki 4 J/cm^2 lazerio energijos kėlimo greitis), antroji zona – dalinai vyksta grūdinimo efektas (nuo 0.25 iki 4 J/cm^2) ir trečioji zona – visada vyksta grūdinimo efektas ($<0.25 \text{ J/cm}^2$).



2 pav. Lazerio indukuotos pažaidos slenksčio rezultatai taikant lokalų lazerio spinduliuotės atkaitinimą su skirtingais protokolais silicio oksido Brego veidrodžiams

Tolimesni LLIA tyrimai parodė, kad maksimali energija, su kuria nanostruktūrizuotas veidrodis gali atlaikyti iki 10000 impulsų į vieną vietą, kol nėra inicijuojamas joks pažeidimas, yra 174 J/cm^2 . Taip pat atlikus ilgaamžiškumo tyrimą, matoma, kad grūdinimo efektas nėra ilgalaikis, t. y. po 100 sekundžių danga vėl degraduoja, jeigu nėra tiesioginės sąveikos su lazerine spinduliuote tame taške. Remiantis šiais tyrimais, iškelta hipotezė, jog kai porėta danga sugeria iš aplinkos vandenį ar kitas daleles, susidaro silanolio grupės, kurios yra įstrigusios į struktūrą. Šios dalelės sugeria lazerinio impulso spinduliuotę, tad esant vienkartiniam didelės energijos lazeriniam impulsui, lokaliai inicijuojami terminiai įtempiai ir danga yra pažeidžiama. Tačiau, jei lazerio impulso energija yra pamažu keliama, silanolio grupės palaipsniui difunduoja nuo lazerio impulso sąveikos su danga kelio, tad lieka tik silicio oksido medžiaga, kuri yra labai atspari lazerinei spinduliuotei.

Kitame poskyryje atliekami tyrimai bendradarbiaujant su lazerio centru Hanoveryje. Atliekami LLIA eksperimentai keičiant aplinkos temperatūrą bei izoliuojant argono dujose (žiūrėti 3 pav.). Iš atliktų matavimų matome, kad dangos argono dujose pasižymi 52 % mažesniu atsparumu lazerinei spinduliutei, o pritaikius papildomą kaitinimą, atsparumas sumažėja daugiau negu 70 %.



3 pav. Silicio oksido Brego veidrodžių LIDT matavimai skirtingose aplinkose ir keičiant temperatūrą

Skulptūrinių dangų pagrindu suformuoti veidrodžiai pasižymi labai aukštu LIDT, tačiau dėl drėgmės optinio elemento spektras gali kisti ir dėl struktūros yra maža sklaida. Norint išvengti šių problemų, galima formuoti nanostruktūrizuotas dangas ant esamo tradiciniu IBS metodu suformuoto veidrodžio, tokiu būdu padidinant šio elemento LIDT. –Kitame poskyryje aprašomas tyrimas, kuriame IBS veidrodis yra padengiamas 4, 10 ir 16 sluoksnių nanostruktūrizuota danga ir matuojamas LIDT pritaikius LLIA metodą. Jau esant 4 sluoksnių dangai matomas LIDT pagerėjimas nuo 7 J/cm² iki 10 J/cm², o esant 16 sluoksnių – LIDT siekia 50 J/cm².

Kitame poskyryje skulptūrinių dangų pagrindu suformuotos dangos yra testuojamos femtosekundinių impulsų lazerinėje sistemoje, esančioje ELI Beamlines, Čekijoje. Buvo suformuoti trys veidrodžiai: ties 800 nm bangos ilgiu 45° kampui – standartinis IBS veidrodis, standartinis IBS veidrodis su papildomais 8 skulptūrinių dangų sluoksniais ir tik skulptūrinių dangų pagrindu suformuotas veidrodis. Atlikti LIDT matavimai naudojant skirtingus protokolus – R-on-1 ir S-on-1, naudojant 120 μm diametro spindulį. Standartinės IBS dangos ir 8 sluoksnių skulptūrinės dangos kombinacija buvo atspariausia lazerio spinduliutei, lyginant su kitais dviem elementais. Eksperimentai atskleidė keletą netikėtų nuovargio efektų ir struktūrinių

pažeidžiamumą nanostruktūrizuotose dangose, todėl siekiant pritaikyti šias dangas femtosekundiniams veidrodžiams būtina atlikti detalesnius tyrimus.

Dangos ant kristalinių padėklų

Šiame skyriuje skulptūrinės dangos yra formuojamos tiesiogiai ant lazerinių kristalų. Pirmajame poskyryje kalbama apie skulptūrinių dangų nusodinimą ant YAG kristalų testuojant veidrodžio zoną 0° kampu ir pralaidumo zoną, pakreipiant bandinį 45° kampu. Pasirinktas bangos ilgis šiuo atveju buvo 532 nm, nes tai yra reikalingesnis ruožas rinkoje. Vienas iš YAG kristalų buvo papildomai nuėsdintas naudojant plazminį šaltinį, siekiant pagerinti paviršiaus kokybę ir padidinti elemento LIDT. Matavimai parodė, kad ėsdinimo procesas pablogino paviršiaus kokybę ir sugeneravo papildomų defektų, o tai lėmė LIDT sumažėjimą – veidrodžio zonoje pasiekė 66 J/cm^2 LIDT, o pralaidumo zonoje nuo 1.56 iki 83.6 J/cm^2 . Tuo tarpu neėsdintas YAG kristalas veidrodžio zonoje pasižymėjo labai aukšta LIDT verte – virš 222 J/cm^2 (tai maksimali lazerio energija), o pralaidumo zonoje nuo 13.5 iki 29.6 J/cm^2 . Iš LIDT matavimų pralaidumo zonoje matome, kad plazminis ėsdinimas turi potencialą, tačiau per didelis defektų generavimas daro labai didelę neigiamą įtaką.

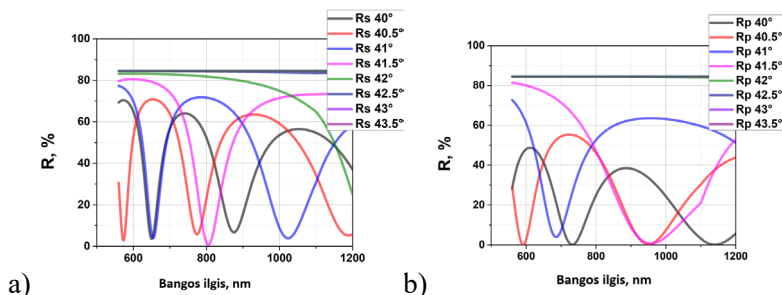
Ėsdintiems YAG kristalams su nusodintomis skulptūrinėmis dangomis buvo papildomai pritaikytas LLIA metodas veidrodžio zonoje siekiant patikrinti, ar įmanoma pagerinti dangų atsparumą. Pritaikius tą patį protokolą, kuris buvo aprašytas ankstesniame skyriuje, buvo pasiekta LIDT vertė iki 140 J/cm^2 .

Visiškas vidaus atspindys YAG kristalams

Šiame poskyryje pristatomas naujas metodas, kaip naudoti skulptūrines dangas visiško vidaus atspindžio taikymams. Naudojant nanostruktūrizuotas dangas, kurios pasižymi mažu efektyviu lūžio rodikliu, galima padidinti visiško vidaus atspindžio efektą YAG kristaluose. Visiškas vidaus atspindys yra taikomas plokščio tipo lazeriams gaminti, tačiau su standartinėmis technologijomis TIR kampas yra iki 55° , naudojant tankų silicio oksido sluoksnį. Nusodinant skulptūrinius sluoksnius su tam tikru efektyviu lūžio rodikliu, galime pasiekti iki 45° TIR efektą (žiūrėti 4 pav.), o tai leistų labai pagerinti plokščio tipo lazerių našumą.

Tam tikri kompleksiniai spektriniai reikalavimai turi būti apsvarstyti formuojant TIR dangą ant YAG kristalo. Siekiant išvengti šiluminio lęšio formavimosi ir dvajopalūžiškumo efektų, dangos turi būti kombinuojamos su

išoriniais aušinimo blokais. Nors TIR efektas gaunamas naudojant tik GLAD dangas, galutiniam produktui yra reikalingos papildomos spektrinės charakteristikos, kurios yra pasiekiamos nusodinant standartines IBS arba EBD dangas ant nanostruktūrizuotų dangų. Dangų nusodinimas kita technologija ant porėtų dangų sukelia papildomas problemas, tad šiame poskyryje atliekama detali spektrinė ir struktūrinė kombinuotų dangų analizė.



4 pav. GLAD dangų teoriškai sumodeliuotas atspindžio spektras a) S poliarizacijai ir b) P poliarizacijai

Pirmiausia dvi YAG prizmės buvo padengtos skulptūriniu 25 sluoksnių danga, kad išpildytų TIR efektą pagal 4 paveikslėlyje sumodeliuotas teorines vertes. Eksperimentiniai matavimai šiek tiek skyrėsi nuo teorinių dėl tam tikrų paklaidų proceso metu bei nuo porėtų dangų efektyvaus lūžio rodiklio pokyčių aplinkoje – vandens absorbcijos. Toliau viena YAG prizmė su skulptūriniu danga buvo padengta IBS danga, o kita – EBD danga, norint palyginti du skirtingus metodus. Abiem atvejais TIR efektas buvo pasiektas tik nuo 46° kampo. Toliau aprašoma detali struktūrinė analizė analizuojant dangų SEM nuotraukas, siekiant išsiaiškinti, kodėl eksperimentiniai duomenys skiriasi nuo teoriškai sumodeliuotų.

Pagrindinė priežastis, lemianti TIR efekto sumažėjimą, yra nanostruktūrizuotų dangų fizinis suspaudimas po papildomos IBS arba EBD dangos nusodinimo ant viršaus. Abiem atvejais iš SEM analizės pastebimas GLAD dangos sumažėjimas dėl sukeltų įtempių. Spektrinė analizė parodė, kad naudotas teorinis porėto silicio efektyvus lūžio rodiklis yra iki 6 % mažesnis negu rodo eksperimento rezultatai. Lūžio rodiklio padidėjimą lėmė dangos suspaudimas bei drėgmės sugertis iš aplinkos. Nepaisant to, naudojant skulptūrines dangas buvo pademonstruotas TIR efekto pagerinimas iki 46° kampo YAG kristalams. Siekiant išvengti atsiradusių problemų, reikalingas papildomas detalus tyrimas su nusodinimo proceso parametrų optimizavimu.

Pagrindiniai rezultatai ir išvados

Vieno sluoksnio dangos naudojant skirtingas medžiagas (Nb_2O_5 , Al_2O_3 , Ta_2O_5 ir SiO_2) buvo nusodinamos skirtingais kampais (0° , 50° , 60° , 70° ir 80°) naudojant GLAD metodą. Dangų porėtumas didėja kartu su nusodinimo kampu dėl šešėliavimo efekto, kaip patvirtinta Brugemano efektyviosios terpės teorija ir SEM vaizdais. LIDT reikšmės skyrėsi priklausomai nuo medžiagos: SiO_2 pasiekė aukščiausias vertes ($>100 \text{ J/cm}^2$ esant mažiems nusodinimo kampams); Al_2O_3 pademonstravo nuoseklų atsparumą lazerinei spinduliuotei ($\sim 32,29 \text{ J/cm}^2$), nepriklausomai nuo porėtumo; Nb_2O_5 ir Ta_2O_5 turi daug mažesnę atsparumą lazerinei spinduliuotei, kur porėtumas turėjo nedidelės įtakos. Defektai, susidarę dangų nusodinimo proceso metu, turėjo didžiausią įtaką LIDT vertėms vieno sluoksnio dangoms.

Silicio oksido daugiasluoksnės dangos buvo suformuotos naudojant GLAD metodą su tankių ir porėtų SiO_2 sluoksnių kombinacija. Porėti sluoksniai sugeria vandenį ar kitas daleles iš aplinkos, sukeliant spektrinius poslinkius ir sumažinant LIDT. Pradinės 1-on-1 LIDT vertės silicio oksido veidrodžiams pasiekė apie 80 J/cm^2 , tačiau po trijų savaičių laikymo atviroje oro aplinkoje sumažėjo iki apie 16 J/cm^2 . Laikant veidrodžius eksikatoriuose arba dujomis užpildytose aplinkose (pvz., argone, azote), LIDT reikšmės stipriai pagerėjo, kai kuriais atvejais buvo pasiekta iki 100 J/cm^2 . Šilumos atkaitinimas ($\sim 200^\circ\text{C}$) iš dalies atstatė LIDT sumažindamas vandens kiekį, o laikymas amoniako terpėje sukėlė cheminę kondensaciją silicio sluoksniuose, tačiau nestabilumą išvengti nepavyko.

LLIA leido palaipsniui didinti lazerio impulso energiją, didinant LIDT iki $180\text{--}200 \text{ J/cm}^2$ Brego veidrodžiuose. Atrodo, kad grūdinimo procesas "išvalė" defektus, pagerindamas porėtų dangų atsparumą lazerinei spinduliuotei. LLIA inertinių dujų aplinkoje pademonstravo geresnius rezultatus nei ore. Tačiau šiluminis kaitinimas LLIA proceso metu sumažino LIDT dėl įtempių įtrūkimų, o tai rodo, kad temperatūra neigiamai veikia stabilumą. SEM ir Nomarski vaizdavimas atskleidė pažeidimų morfologijas, susijusias su įtempiais ir dalelių sugertimi. Porėtos struktūros buvo atsparios šiluminiam plėtimuisi, tačiau buvo pažeidžiamos dėl drėgmės ir įtempių sukeltų įtrūkimų. Dangų laikymas kontroliuojamoje aplinkoje (pvz., argone ar azote) ir taikant LLIA protokolus su lėtu energijos didinimu ($0,125 \text{ J/cm}^2$ kiekvienam impulsui) parodė daugiausiai perspektyvų išlaikyti optinį našumą laikui bėgant.

Siekiant pagerinti veidrodžių LIDT, buvo sukurtos hibridinės daugiasluoksnės dangos, kombinuojant IBS ir GLAD technologijas. Pademonstruotas pagerintas atsparumas, pasiekiant LIDT vertes iki 47 J/cm^2

hibridiniams silicio oksido veidrodžiams po LLIA. Ši technika efektyviai suderino maža sklaida pasižyminčius ir aukštą atsparumą lazerinei spinduliuotei turinčius sluoksnius.

Silicio oksido dangos buvo testuojamos femtosekundinių lazerių sistemose ir pasiekė aukštesnes LIDT reikšmes nei tradicinės IBS dangos. Tačiau tam tikromis sąlygomis buvo stebimi netikėti nuovargio efektai ir struktūriniai pažeidžiamumai, ypač nanostruktūruotose porėtose silicio dangose.

Nanostruktūrizuotos silicio oksido dangos buvo pritaikytos YAG kristalams, pasiekiant aukštas LIDT vertes: 222 J/cm^2 nešdintiems kristalams ir iki 140 J/cm^2 plazma-ėsdintiems kristalams naudojant LLIA. Plazma-ėsdinti paviršiai pasižymėjo didesniu defektų kiekiu, todėl LIDT sumažėjo.

GLAD dangos buvo naudojamos optimizuoti YAG kristalų TIR konfigūracijas ir pasiekti net 46° efektyvų atspindžio kampą. Tačiau teorinių ir eksperimentinių rezultatų neatitikimai išryškino tokius iššūkius kaip nanostruktūrinis slopinimas ir aplinkos vandens sugertis. SEM parodė, kad GLAD dangų storis sumažėjo, o efektyvus lūžio rodiklis padidėjo, kai ant jų buvo nusodinamos papildomos dangos naudojant IBS arba EBD metodus. Porėtos silicio oksido dangos vandens sugertis sukėlė lūžio rodiklio pokyčius iki 3%, o tai turėjo įtakos spektrinėms charakteristikoms.

PADĖKA

Visų pirma norėčiau padėkoti savo šeimynai – mylimai žmonai, mano mamai ir tėčiui ir žinoma šuniukui Tango, už nuolatinį palaikymą, pasitikėjimą ir už tai, kad neleido pasiduoti. Ačiū Audronei už lietuvių kalbos pamokas rašymo metu ir skirtą laiką.

Ypač noriu padėkoti savo moksliniam vadovui dr. Tomui Toleniui už rūpestį, pastabas ir įžvalgas bei už tai, kad būdamas kitoje šalyje negailėdavo man laiko. Už suteiktas žinias, patirtį ir supažindimą su skulptūrinių dangų tematika.

Taip pat noriu padėkoti kitiems FTMC optinių dangų laboratorijos darbuotojams, ypač dr. Linai Grinevičiūtei, dr. Ryčiui Buzeliui, dr. Simui Melnikui, dr. Giedriui Abromavičiui, Linai Volosevičienei, Julianijai Nikitinai ir visiems kitiems nepamintiems kolegoms už galimybę dirbti jaukioje aplinkoje.

Noriu padėkoti kolegoms iš ELI Beamlines ir Laser Zentrum Hannover už bendradarbiavimą ir suteiktą galimybę naudotis jų įranga, kad gauti rezultatus, kurie aprašyti disertacijoje.

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AWARDS

- 2021.10.12 – 2021.10.15 SPIE.Laser Damage MJ Soileau 2021 Best Student Paper Award

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