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Laser modification of PbSe chalcogenide films via LIPSS formation

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Abstract. The study investigates the laser modification of lead selenide (PbSe) chalcogenide films with the formation of laser-induced periodic surface structures (LIPSS). These modifications are crucial for enhancing the sensitivity of gas analyzers, particularly in detecting hazardous gases in various industries. The use of nanosecond laser pulses for film processing offers improved productivity, better reproducibility, and greater control over optical properties compared to conventional furnace annealing techniques. The formation of LIPSS under specific laser irradiation conditions leads to changes in the film's optical characteristics, including increased absorption in the infrared (IR) range. Additionally, the study examines the dependence of the periodicity of these structures on the power density of the applied laser radiation. The findings highlight the potential of laser modification for creating new optical properties and developing innovative photonics devices.

Keywords: PbSe films, laser modification, optical characteristics, nanosecond laser pulses, laser-induced periodic surface structures (LIPSS)

Introduction

Laser-induced periodic surface structures (LIPSS) have emerged as a powerful tool for modifying the surface properties of materials, enabling precise control over optical, mechanical, and chemical characteristics (Bonse 2020). These nanostructures, typically formed through the interaction of laser radiation with a material's surface, have found applications in a wide range of fields, including photonics, tribology, and biomedicine (Antipov et al. 2012; Bonse 2020). The ability to tailor surface properties at the micro- and nanoscale makes LIPSS particularly attractive for developing advanced optical devices, sensors, and functional coatings.

One of the key advantages of LIPSS is their ability to enhance optical properties of materials, such as increasing absorption in specific wavelength ranges or creating diffraction effects. This is especially relevant for materials like lead selenide (PbSe), which exhibit high photosensitivity in the infrared (IR) range (Tan, Mohseni 2018). PbSe films, widely used in photodetectors and gas sensors, can benefit significantly from laser-induced modifications (Nielsen et al. 2023; Peng et al. 2022). Conventional furnace annealing of PbSe films is hindered by high defect densities, elevated production costs, and poor process repeatability. These limitations have motivated the development of laser-based surface modification techniques as a promising alternative (Tan, Mohseni 2018).

The formation of LIPSS on PbSe films not only enhances their IR absorption, but also opens up new possibilities for creating innovative photonic devices, such as diffraction elements and sensors with tailored optical responses (Gupta et al. 2021). Compared to conventional furnace annealing, LIPSS formation can significantly improve reproducibility and offer more dynamic control over the material's optical properties (Nielsen et al. 2023; Olkhova et al. 2023).

In this study, we investigate the formation of LIPSS on PbSe chalcogenide films using nanosecond laser pulses. The focus is on understanding the mechanisms behind LIPSS formation and their impact on the optical properties of films. By exploring the relationship between laser parameters (e. g., power density, pulse duration) and the resulting surface structures, we aim to demonstrate the potential of laser modification for developing new optical materials and devices. This work highlights the broader applicability of LIPSS in material science and photonics, paving the way for future advancements in surface engineering and optical technology. The formation of LIPSS on the surface of PbSe films can allow more controlled modification of the material and obtain new optical properties (Nykyruy et al. 2019; Olkhova et al. 2022), as well as the creation of diffraction elements by direct laser writing, which represents the potential for the creation of new photonics devices.

Materials and methods

The 0.6 μm thick polycrystalline PbSe films used in this work were created by vacuum-thermal sputtering on a plane-parallel substrate made of 0.2 mm thick cover glass. The film samples were fabricated by Optosens LLC, Russia.

Laser modification of the structure and properties of the films was performed by nanosecond pulses of a fiber Yb laser based on the Minimarker-2 complex (Laser Center LLC, Russia) with a wavelength of 1064 nm and a Gaussian profile of energy distribution in the beam cross-section. Spot's movement was controlled using a two-mirror galvanometer scanner. After the scanner mirrors, the beam was focused by an F-theta lens with a processing field of 100x100 mm on the film surface, where the spot diameter was 50 μm. The polarization of the radiation incident on the sample was adjusted using a Glan-Taylor prism and a half-wave phase plate (Fig. 1). The following parameters were used to determine the modes of LIPPS formation: pulse duration (from 14 to 100 ns), average power (from 100 to 500 mW), and pulse repetition rate (from 30 to 140 kHz). At the same time, the laser spot scanning speed remained unchanged and equal to 15 mm/s, which provided an overlap of more than 0.99. The modes of sample modification using laser radiation are presented in Table 1.

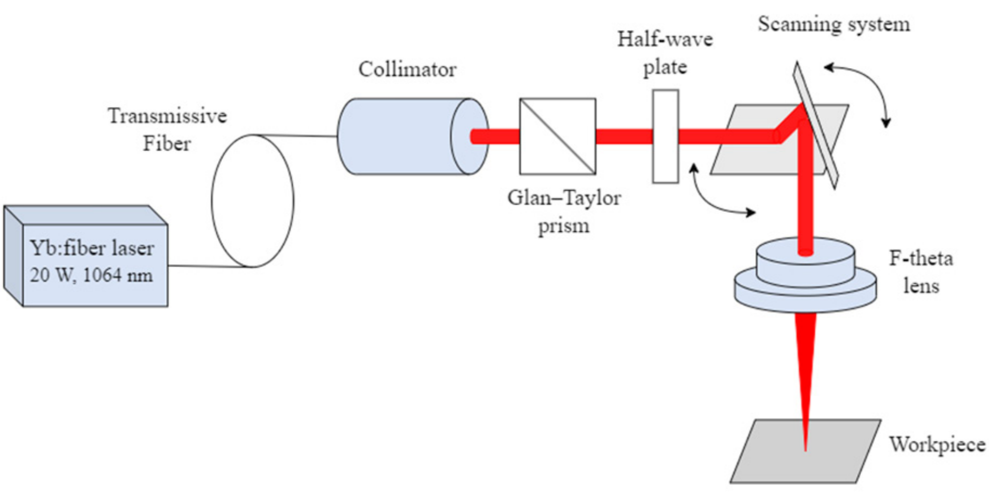

Fig. 1. Schematic diagram of the experimental setup for laser processing of chalcogenide films with LIPPS formation

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Table 1. Modification modes of chalcogenide film using a pulsed laser source with a wavelength of 1064 nm

No	Pulse duration, ns	Frequency, kHz	Average power, W	Power density, kW/cm^2
1	100	60	0.271	11.81
2	50	90	0.299	13.52
3	20	90	0.29	16.77

The structures obtained on the sample were investigated by optical microscopy in the light and dark fields of transmitted and reflected light using a Carl Zeiss Axio Imager microscope (Germany). Spectral reflection and transmittance of periodic structures in linearly polarized light at different angles of sample rotation were measured using a spectrophotometer MSFU-K Yu-30.54.072, LOMO (Russia) in the wavelength range between 380 and 900 nm. The period of the structures was determined via the analysis of optical microscopy data by two-dimensional fast Fourier transform (2D-FFT) using the open-source software Gwyddion (Version 2.62).

Scanning electron microscopy (SEM) was performed using a Merlin Zeiss high-resolution electron microscope (Germany) to evaluate the modification of the film structure after laser exposure.

Results and Discussion

Structure modification

In contrast to the traditional heat treatment in the furnace, the method of laser modification of the film structure is characterized by the localization of thermal influence with a high temperature gradient in the center and at the edges of the irradiation zone. During laser exposure, darkening of the film was observed due to changes in the intermolecular bonds of PbSe in the area of exposure (Olkhova et al. 2023). The darkening of the film led to an increase in the absorption capacity and thus to an increase in the fraction of the absorbed incident radiation energy, which influenced the temperature change in the laser-modified region.

Obtained LIPSS were investigated by optical microscopy and 2D-FFT. The formation of periodic structures, classified as Low Spatial-Frequency LIPSS (LSFL) (Bonse 2020), with a period of 0.7 ± 0.1 μm and with a period of 1.2 ± 0.2 μm (Fig. 2), occurred during laser exposure of the film.

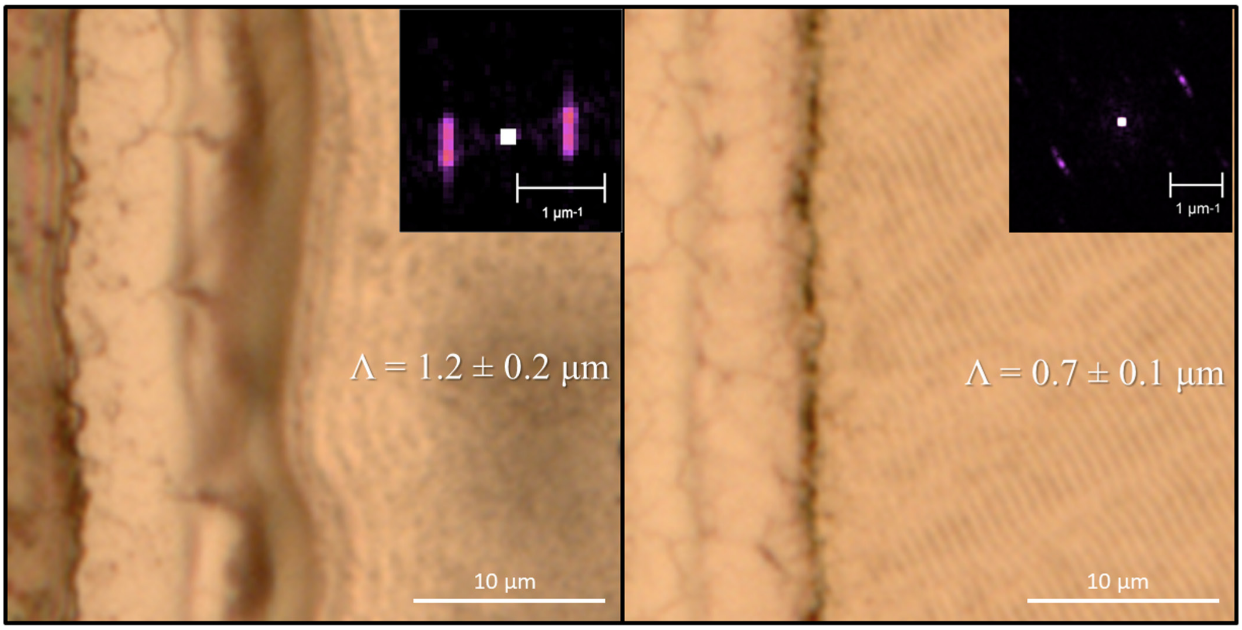

Fig. 2. Optical microscopy and 2D-FFT results of tracks exhibiting LIPSS with periods of 0.7 (power density of 16.77 kW/cm^2) and 1.2 μm (power density of 11.81 kW/cm^2)

The periodic structures with 0.7 μm spacing were formed in power density ranges of 14 kW/cm^2 and higher. At lower power densities in the range of 10 kW/cm^2 to 12 kW/cm^2, the structure period increased to 1.2 μm (Fig. 3)

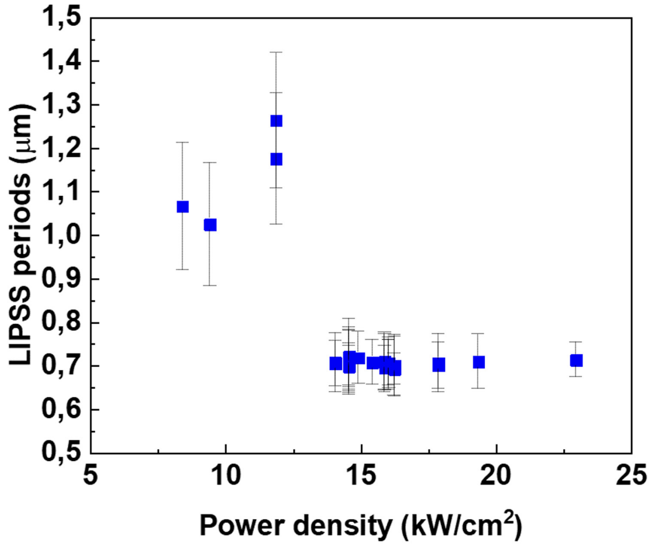

Fig. 3. Power density dependence of LIPSS periodicity

The formation of laser-induced periodic structures (LIPSS) on PbSe films under nanosecond exposure is associated with thermal and hydrodynamic processes depending on the laser power density. In the 'non-through oxidation' regime (7.5–12.5 kW/cm^2), the structures were formed predominantly at the edges of the laser exposure track, repeating its contour, with a period of 1.2 ± 0.2 μm. This is explained by local softening of the material, formation of a melt bath, and subsequent formation of a 'border' due to thermo-capillary flows (Marangoni effect). Diffraction of laser radiation on edge rolls led to the formation of periodic structures parallel to the roll.

With increasing power density ('through oxidation' mode), the structures appeared across the entire track width, aligning with the laser radiation polarization and demonstrating a smaller period — 0.7 μm. This value agrees with the dependence $\Lambda \approx \lambda/n_{substr}$ (Bonse 2020), where $n_{substr} = 1.5$ for a glass substrate $\lambda = 1064$ nm, $\Lambda \approx 710$ nm.

'Non-through oxidation' is characterized by the use of shorter nanosecond pulses and lower power density, at which LSFLs of a larger period are predominantly formed (Olkhova et al. 2023). Increasing the pulse duration as well as increasing the power density leads to a decrease in the LSFL period as a result of reaching 'through oxidation' (Olkhova et al. 2023).

Figure 4 shows photographs of the modified region. The structures have a period of 0.7 μm throughout the scanning track, which was confirmed by the 2D-FFT spectrum (Fig. 4a). When viewed in transmitted light, LSFLs formed on the initially opaque PbSe film can be seen, which confirms the assumption that 'through oxidation' was achieved during processing (Fig 4b). SEM results (Fig 4c) confirm inhomogeneous character of surface oxidation (Fig 4d).

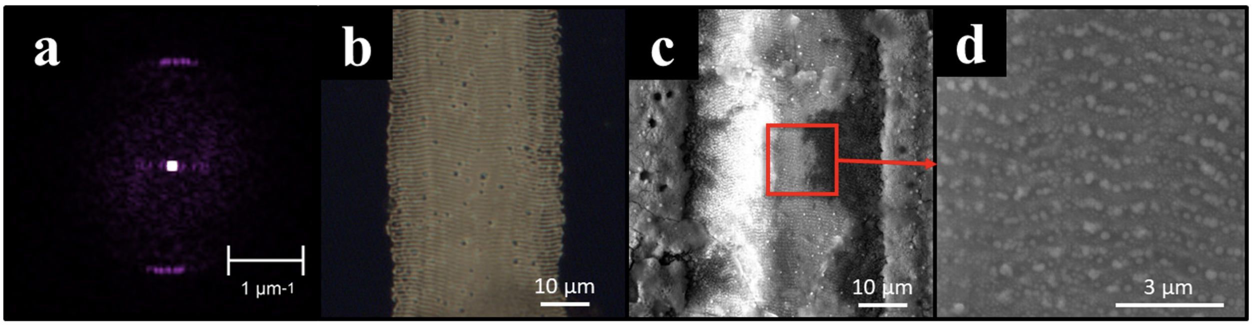

Fig. 4. (a) FFT spectrum of the LSFLs with $\Lambda = 0.7$ μm and their microphotographs obtained (b) by transmitted light optical microscopy and (c, d) by SEM (pulse duration 20 ns, frequency 90 kHz, power density 16.77 kW/cm^2)

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Optical properties

Following laser recording, the optical properties of the periodic structures were examined. Transmission and specular reflection spectra of linearly polarized light were measured at varying rotation angles of the structures.

The most significant angles were 0° and 90°, corresponding to orientations where the periodic structure lines were aligned parallel and perpendicular to the light polarization direction, respectively.

Reflectance spectra of the film before and after laser irradiation show that the reflectance of the modified region decreases due to laser exposure (Fig. 5). The spectra of modified LSFL regions with a period of 0.7 μm exhibit a rise in the 780–810 nm range and a dip in the short-wavelength region. When the period increases to 1.2 μm, the rise in the IR region vanishes, while reflection in the short-wavelength region increases. In all cases, reflection is higher when the polarization vector is aligned with the LSFL lines; rotating the polarization vector by 90° leads to a slight decrease in reflection across the entire measured spectrum. This spectral dependence arises from two factors: (1) the presence of submicron surface relief in the form of periodic structures and (2) a reduction in the refractive index of the near-surface PbSe film layer due to oxidation (Olkhova et al. 2023). The observed artificial anisotropy is a notable phenomenon, more commonly associated with femtosecond laser surface modification (Kolchin et al. 2022). Its occurrence after nanosecond pulsed treatment may suggest the induction of phase transitions.

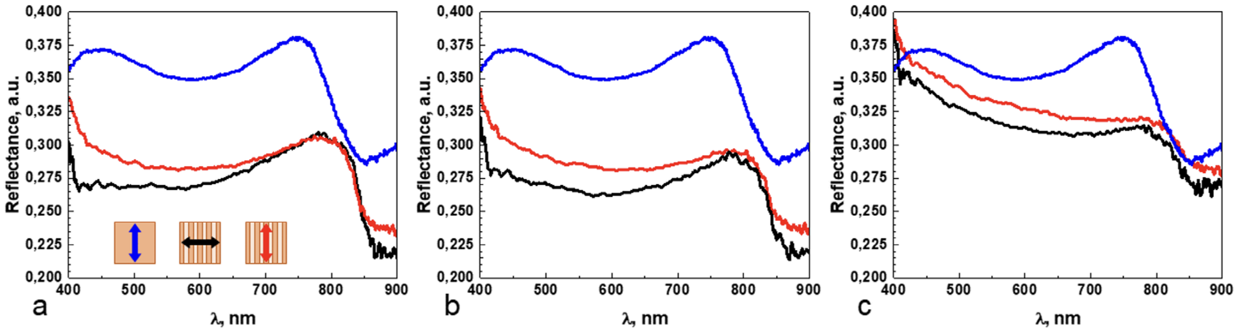

Fig. 5. Reflectance spectra of PbSe films obtained for samples treated with different pulse durations: (a) 20 ns (16.77 kW/cm^2), (b) 50 ns (13.52 kW/cm^2), (c) 100 ns (11.81 kW/cm^2), for different rotation angles of periodic structures in polarized light

The reflection maximum near 750 nm, characteristic of the unmodified PbSe film, redshifts and broadens into the 780–810 nm range after laser exposure. Varying degrees of film oxidation may alter the refractive indices and introduce optical quenching, consequently reducing the film's reflectance. The observed redshift of the maximum into the infrared region results from diffraction effects of waves reflected from the periodic structure (Chourasia et al. 2024).

Following laser modification, the film's transmittance in the visible spectrum increased to 23–25% (Fig. 6), attributed to film oxidation and thickness reduction (Olkhova et al. 2023). Notably, the pristine PbSe film exhibits no transparency in the visible spectral range. Rotation of the polarization vector relative to the LSFL lines showed negligible impact on transmitted light intensity, with only minor variations observed in the 780–810 nm region. These effects are likewise associated with film oxidation (Chourasia et al. 2024).

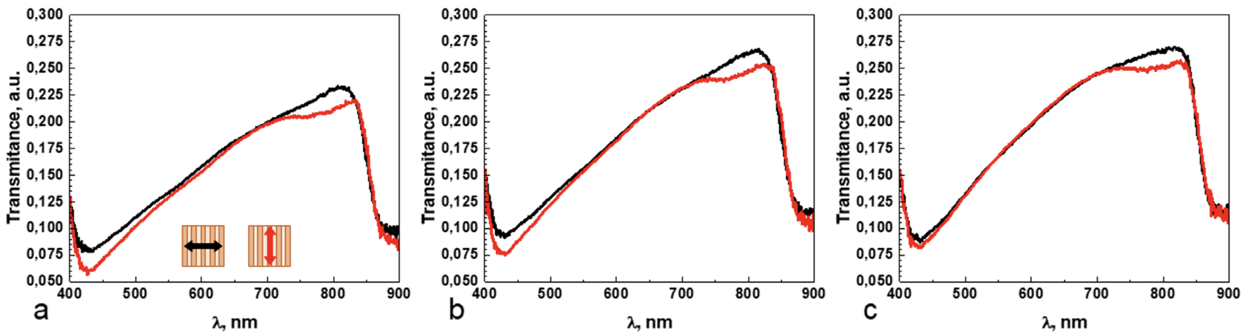

Fig. 6. Transmission spectra of PbSe films obtained for samples treated with different pulse durations: (a) 20 ns, (b) 50 ns, (c) 100 ns for different rotation angles of periodic structures in polarized light

Conclusions

The study has identified the formation modes of LIPSS on thin PbSe films under nanosecond laser irradiation. We observed a dependence of the structure periodicity on irradiation parameters. Large-period structures exhibit surface modification resulting from localized material softening and the Marangoni effect, consistent with a 'non-through oxidation' mode.

Notably, we detected a redshift of the local reflection maximum from 750 nm to 780–810 nm in samples with 0.7 μm period structures. Spectral analysis revealed that variations in transmission and reflection spectra for different polarization orientations relative to the lattice lines remain within 2%. Furthermore, treated PbSe films showed increased reflectance up to 25% in the modified regions, attributable to both film thinning and oxide layer formation.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors discussed the final work and took their respective part in writing the article.

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