FEMTOSECOND LASER PROCESSING OF TITANIUM DIOXIDE FILMS FOR PHOTOCATALYTIC AND SELF-CLEANING APPLICATIONS

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Introduction Titanium dioxide (TiO_2) layers on various substrates are interesting for their self-cleaning and photocatalytic properties that are crucial for removing organic compounds of biological origin from optical elements operating in harsh environmental conditions. TiO_2 is of particular interest due to its multiple polytypes (brookite, anatase and rutile) which can transform into one another. We present the development of functional TiO_2 films on glass substrates and their subsequent processing with femtosecond laser radiation. The femtosecond laser treatment provides fast and reliable method for contactless modification of thin films. Laser treatment of TiO_2 films offers broad opportunities to tailor film characteristics such as thickness, crystalline or amorphous structure, grain size, residual stress, and defect density. [1]

Methods of the preparation and further treatment of TiO_2 films The TiO_2 sols have been synthesized using the sol-gel method. TiO_2 film preparation included applying a sol onto glass substrates using spin-coating method followed by drying and calcination at 450°C. Annealing regime was selected to improve film density and uniformity. Further modification was performed using ultrashort laser pulses generated by a Ti:sapphire laser system (λ = 800 nm, the pulse repetition frequency 1kHz, the pulse duration ~ 100 fs, scanning velocity 3 mm/s).

Results

- SEM analysis the ${}_2TiO$ film on glass substrate reveals satisfactory uniformity of TiO_2 film (Fig. a, b), and moreover good dielectric properties.

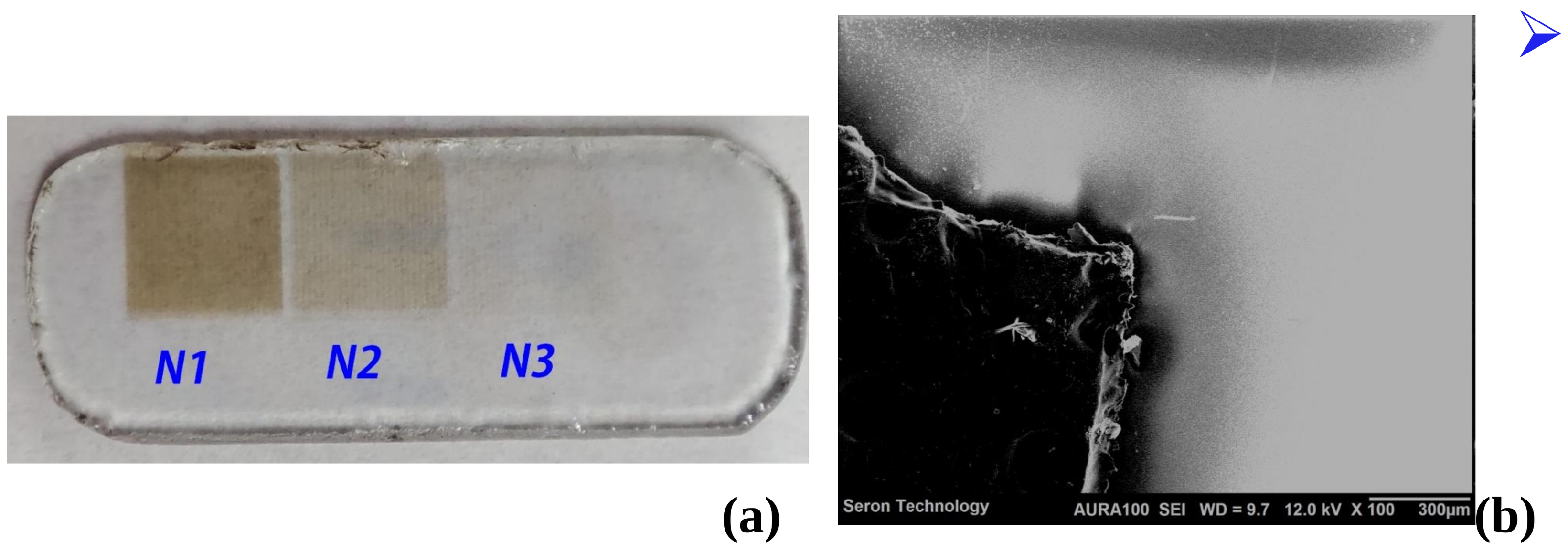

Fig. 1. (a) View of the sample with TiO_2 film with marked areas treated with a femtosecond laser (fundamental wavelength 800 nm). (b) SEM image of the TiO_2 film.

- Before calcination, the TiO_2 film (thickness of 247 nm) is porous with significant roughness. After calcination, the TiO_2 film becomes significantly thinner (~ 90 nm) and denser. Initial laser-induced periodic surface structures (LIPSS), nanoparticles, nano-cracks, and other features have been revealed after the treatment with linearly polarized femtosecond (fs-) laser irradiation with λ=800 nm, the pulse irradiation energy density was in the range of 0.225 – 0.025 $J \cdot cm^{-2}$ that resulted in different transparency of the TiO_2 film (areas N1-N3, respectively). Femtosecond laser fluence have been selected near the ablation threshold. As it is seen from Fig. 1, femtosecond laser treatment parameters were selected to preserve sufficient transparency of the TiO_2 film. The laser treated area of TiO_2 film demonstrated hydrophilic properties.

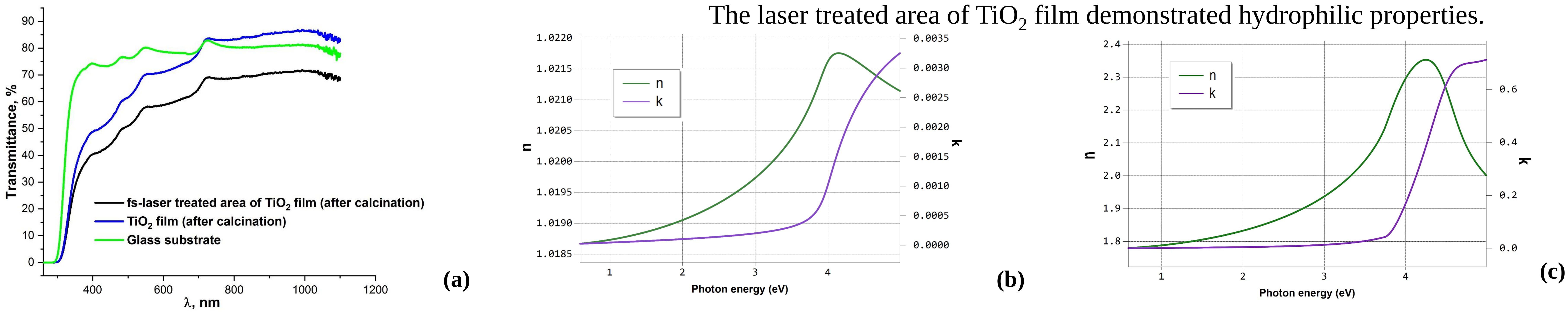

Fig. 2. (a) Transmittance of glass substrate and TiO_2 films after calcination at 450°C, (b) Spectral dependences of optical parameters of TiO2 films before (a) and after (c) calcination at 450°C.

- The films exhibit a large energy band gap of 3.9 eV before calcination, which decreases slightly to 3.7 eV after calcination. Since no conducting component is detected, this band gap value for TiO2 may be due not to the Burstein-Moss effect, but to the quantum-size effect.

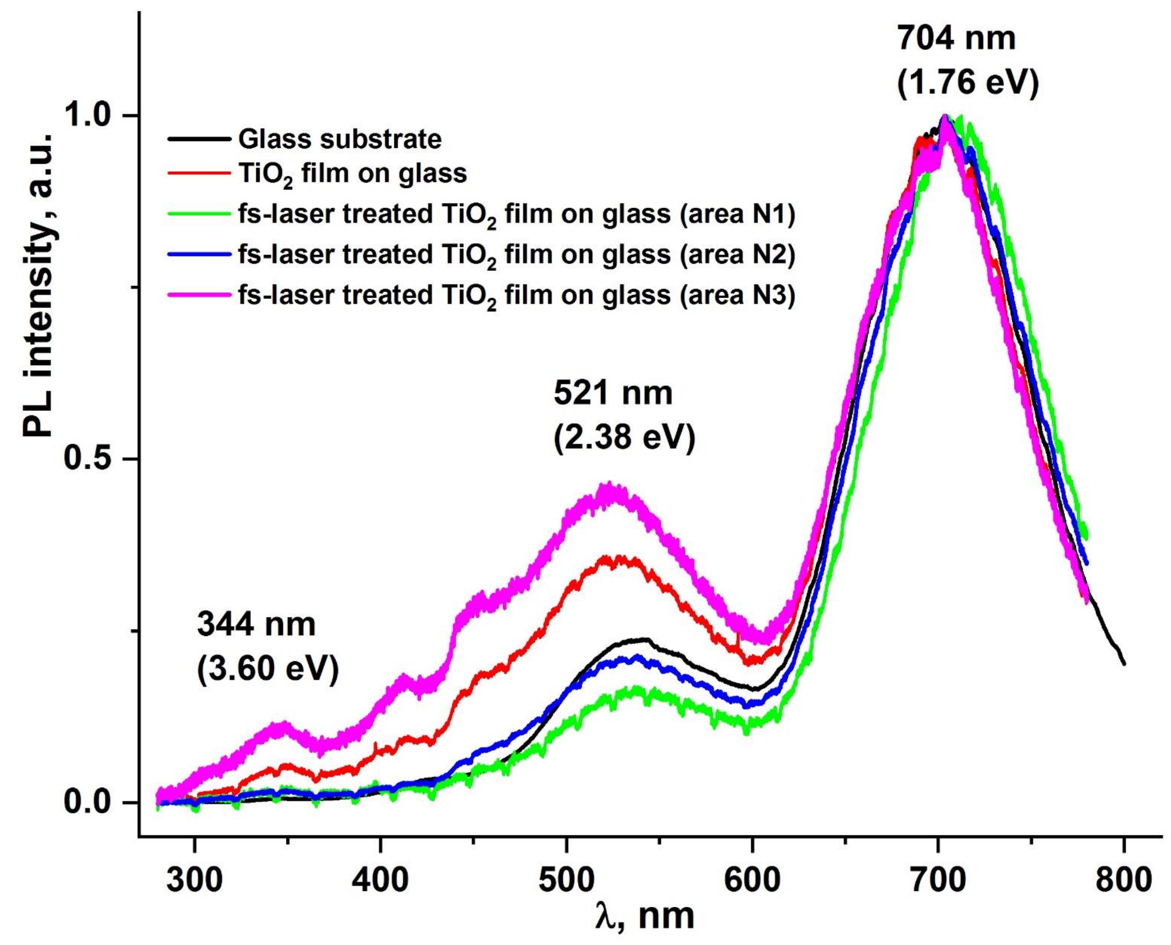

Fig. 3. PL spectra of glass substrate and TiO_2 films before and after laser treatment.

- Photoluminescence (PL) spectra have been studied for each regime of femtosecond laser treatment of TiO_2 films deposited on glass. PL intensity presents the recombination efficiency of photogenerated charges that is an important factor for photocatalytic efficiency of TiO_2 films. PL spectra of TiO_2 films (both as grown and laser-treated) contain some intense broad PL bands. Emission from the glass substrate contributes to PL of the samples, namely causing the appearance of bands at about 536 nm (2.31 eV), 704 nm (1.76 eV). Nature of PL bands related to TiO_2 films can be defined as follows: wide complex band at around 521 nm (2.38 eV) is associated with the transitions from shallow trap levels induced by the presence of the oxygen vacancies, and weak broad PL band at about 344 nm (3.6 eV) corresponds to recombination of free and bound excitons in TiO_2. The relative intensities of these bands depend significantly on the parameters of laser processing of TiO_2 films.

CONCLUSIONS: **The development of functional TiO_2 films on glass substrates and their subsequent processing with femtosecond laser radiation have been studied. We demonstrated the femtosecond laser treatment conditions that satisfactory preserved sufficient transparency of the TiO_2 film that is perspective for the coating of optical elements of special devices. The transparent laser treated area of TiO_2 film demonstrated hydrophilic properties, and PL spectrum of TiO_2 film at the pulse irradiation energy density of 0.225 $J \cdot cm^{-2}$ contains main features of PL spectrum of as-grown TiO_2 film.**

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Acknowledgments: *Authors appreciate funding from the National Research Foundation of Ukraine (Project No.* 2025.06/0087 (Agreement No. 209/0087) *“Nanostructured titanium dioxide films for coating of optical elements”).*

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