Optical spectra of titanium modified surfaces with LIPSS and gold nanoparticles

A Khankaev1*, A Tcibulnikova1*, V Bryukhanov1*, I Samusev1*, M Demin1, I Lyatun1.
1Immanuel Kant Baltic Federal University, 1SEC Fundamental and Applied Photonics. Nanophotonics, Kaliningrad 236016, Russia

Abstract. This paper presents the reflection spectra of s- and p-polarized light and the refractive index spectra of anodized titanium surfaces modified by laser-induced periodic structures with gold nanoparticles. It is shown that these surfaces generate surface plasmons in the visible region of the spectrum, which leads to the formation of a negative values region in the refractive index.

1. Introduction.
Since Birnbaum's first observation of laser-induced surface structures [1] ultrashort pulse lasers have reached a high level in terms of their technical capabilities. Modern lasers are able to create such structures in a single step in the range of up to 100 nm. Such abilities attract the attention of a large number of researchers, because the creation of metal nanostructures is a way to control their optical, physical and chemical properties. Thus, micro/nano periodic structures on the copper surface under femtosecond laser exposure are currently being studied in [2]. The authors have been shown that varying the defocusing distance, laser power and scanning speed leads to the changes in the size of fusiform structures on the surface. The properties of laser induced periodic surface structures (LIPSS) on the titanium surface were studied in [3] when the number of radiating pulses and the environment of the laser path beam (air, water) were changed. The paper reveals the appearance of periodic structures of several tens of nanometers in size, oriented parallel to the laser beam. Other studies of LIPSS are also known [4-6]. Thus, the formation of LIPPS occurs under femtosecond laser exposure, and the properties of these structures depend on the laser parameters such as laser polarization, pulse energy, angle of incidence and the properties of the medium and material. LIPPS allow to change the optical, biological, mechanical properties and wettability of the modified surfaces. The possibility of using LIPPS in physics, chemistry, medicine and biology makes these structures a promising area of research due to the plasmons generation on these structures [8-10]. This paper presents a study aimed to investigate the formation of LIPPS on the anodized titanium surface with gold nanoparticles (NPs) and changes in its optical properties in visible and near IR-region.

2. Materials and methods

2.1. Femtosecond LIPSS fabricating
Avesta femtosecond laser (THETA-25/30 laser system, Russia) with a wavelength radiation of \( \lambda = 1032 \) nm (pulse duration of 280 fs and a frequency of 25 kHz) operating in a quasi-continuous mode was used for fabricating LIPSS on titanium surfaces. The titanium plate was mounted on a motorized positioner 8 MTF-102LS05 (Standa, Lithuania), controlled by XILab software. When forming
periodic structures, the laser radiation energy was 12.5 mkJ. The structures were fabricated as a bands at equal distances from each other under speed scanning of 200 mkm/s. Gold nanoparticles were also synthesized on this fs laser unit according to the method described in detail in [11]. The obtained gold nanoparticles were deposited on titanium surfaces with LIPSS.

2.2. Optical measurements
The reflectance and refractive index spectra of titanium surfaces after laser exposure were measured on the AUTO-SE spectroscopic ellipsometer (HORIBA and Jobin Yvon, France). The morphology of titanium LIPSS was investigated by means of Zeiss Cross Beam-540 (FIB-SEM) electron microscope.

3. Results and discussion
As known, the structure of a metal surface largely determines its physical and optical properties. The processes of plasmon generation on rough metal surfaces and the plasmons energy transfer to the dye and biological molecules have been considered in our previous works [12, 13]. Creating structured surfaces with a certain properties is a rather difficult task. Thus, it was already shown that the modification of titanium and silver surfaces by anodization methods leads to the appearance of nonlinear optical effects in the spectra of dielectric permittivity functions, absorption and reflection [14]. This paper presents an investigation of the plasmon spectra of titanium surfaces modified by femtosecond infrared laser radiation.

In the first series of experiments, SEM images of titanium surfaces before and after laser structuring and deposition of ablative gold nanoparticles were studied. Figure 1 presents the morphology of titanium surfaces before and after femtosecond laser exposure.

![Figure 1](image1.png)

**Figure 1.** SEM images of anodized titanium surface without laser treatment (a); the path beam fabricated by laser radiation (b); morphology of structures within the band (c); peripheral area near the band (d).
Thus, figure 1a shows the titanium surface before laser exposure. Figure 1b shows an image of LIPSS at a scale of 20 mkm and the inset shows the surface morphology at a scale of 200 nm. As can be seen in figure 1b the width of the laser beam on the titanium surface is ≈ 1 µm. The distance between the bands is ≈ 95 µm. There is also an agglomeration of titanium particles near the band, fabricating during the laser ablation of the titanium surface and settle on the surface. These clusters of titanium particles (figure 1c) represent a rough surface that covers an area with a width of ≈ 20 mkm from the center of the band. Figure 1d shows this surface at a scale of 200 nm. From this image, it can be concluded that the surface formed by particles is a hill-like formation.

Gold nanoparticles were deposited on the titanium surface with LIPSS (figure 1b, insert). The average diameter of nanoparticles according to the SEM images is 60-70 nm. Thus, the femtosecond structuring of the titanium surface leads to the formation of structures of different landform and different roughness.

Next, it was interesting to consider the optical spectra of the obtained surfaces. Figure 2 shows the reflection and refractive index spectra of titanium nanostructured surfaces with gold nanoparticles.

![Figure 2](image)

**Figure 2.** Reflectance spectra (a, b) and refractive index spectra (c) of anodized titanium surface modified by gold nanoparticles without LIPSS (solid curves) and with LIPSS (dot curves).

As can be seen from figure 2 (a,b), two minima are observed in the reflection spectra. The first minimum, located in the region of 550-600 nm, is due to the plasmon resonance of gold nanoparticles. The second minimum in the region of 650-700 nm is due to the plasmon resonance generated on the laser-structured surface of titanium. Minima of the reflection spectrum of p-polarized radiation of the titanium anodized surface with deposited gold nanoparticles are located at the wavelength of 540 nm and 679 nm. For s-polarized radiation, a broadening of the spectrum is observed in the plasmon resonance region of nanoparticles. The value of the reflection coefficients of s-polarized radiation for the plasmon resonance of gold NPs on a surface without LIPSS and with LIPSS is 0.26 and 0.35, respectively. Note that the position of the minima of the absorption spectrum of the titanium surface does not change and is shifted to the blue region after laser exposure. The values of the coefficients Rp and Rs at λ=650 nm (for the surface of titanium with LIPSS and gold nanoparticles) are the same.

As can be seen from figure 2c, a region of negative refractive index values is observed in the refractive index spectrum (600-800 nm). This region corresponds to the region of surface plasmon generation on the titanium surface with LIPSS. There is a strong absorption of incident radiation by surface nanostructures in this wavelength region. Absorption caused by gold nanoparticles and nanostructures formed by laser exposure on the titanium surface (figure 1b) leads to spectral summation of the refractive index spectra and forms a region of negative n values. Note that the region of negative values of the refractive index is of particular interest at present time in connection with the study of metasurfaces [15, 16]. Therefore, further studies of laser nanostructured surfaces will also be
connected with modeling of the refractive index in the visible region of the spectrum and selecting a theoretical model to describe the function $n(\lambda)$ in the negative region on a rough surface of various roughness.

4. Conclusions
In this paper, it is shown that laser femtosecond exposure to an anodized titanium surface can form nanostructures of various morphologies with certain optical properties. Modification of the titanium surface by LIPSS leads to the local minimum in the reflection spectra of $p$- and $s$-polarized radiation and a region of negative values in the refractive index spectrum. These processes are caused by plasmon fluctuations of electron density generated on metal nanostructures of the surface.

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