Transformation of refractive index spectra for titanium rough surfaces

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ABSTRACT

Optical properties (reflection, refractive index, real and imaginary part of permittivity function) of rough titanium surfaces fabricated by anodizing method at different anodic voltage have been studied. It is shown that a negative region in the visible wavelength range is observed on a rough titanium surface in the refractive index spectrum; its minimum appeared to be red-shifted with surface roughness increase. These optical-nonlinear effects are studied by means s- and p-polarized light reflection coefficients spectra and permittivity spectra registration. It is also shown that the generation of surface plasmon oscillations in the visible spectral region on the rough titanium surface is possible. Excitation of surface plasmons is found to be accompanied by redistribution of the incident electromagnetic energy on the surface and leads to various nonlinear effects including negative values of the refractive index.

Keywords: negative refractive index, plasmon generation, visible wavelength range, anodic dissolution, reflection, dielectric permittivity, titanium rough surface

1. INTRODUCTION

Nowadays, titanium-based materials are widely used in medicine [1, 2], photovoltaics and optoelectronics [3]. Due to their high biocompatibility and titanium osteointegration, they are made use as implants [4]. Owing to unique physical and chemical properties, pure titanium as well as titanium oxide of various phase composition can be integrated into electro-chemical schemes of optical sensors and solar energy conversion devices [5]. Particular attention has been paid to the titanium nanoparticles (NPs) of different shape (nanotubes, nanowires etc.) which are synthesized by means of titanium surface anodizing [6]. Structural and optical properties of these media are actively investigated by novel spectral methods [7, 8].

At the same time, the optical properties of such oxide nanostructures on the titanium surface are closely associated with a number of photophysical processes of incident electromagnetic energy conversion at the metallic titanium interface.

The study of rough metallic surfaces (i.e. gold and silver) is closely related to the surface plasmon oscillations generated on them [9, 10]. It is known that interaction of incident electromagnetic radiation with rough metal surface can be described by the surface complex dielectric permittivity function distribution \( \varepsilon(\lambda) \) [10]. The presence of an oxide layer of a nanometer-scale results in significant changes in the \( \varepsilon(\lambda) \) spectrum for surface plasmons.

It is important to notice that the oxide film and anodic dissolved titanium surface are considered to be a single composite medium, in which the processes of the incident electromagnetic radiation transformation take place as a result of metallic structure – oxide film interaction.

Thus, in this paper, we aimed to identify the spectral changes in complex dielectric permittivity of the rough anodized titanium surface – TiO\(_2\) interface as a result of the surface structure change. We also determined the contribution of plasmonic oscillations into the total spectral properties of the complex dielectric permittivity function and the refractive index of the anodized titanium surface.

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2. EXPERIMENT

The titanium plates anodizing technique was performed according to the method presented in detail in [11]. We used the titanium plates with a width of 0.1 mm as electrodes. The samples were anodized in 5% KOH solution in potential-static mode at a voltage of 30 V on electrodes for three minutes. Titanium anodic oxidation resulted in rough surface covered with TiO$_2$ formation. Immediately after anodizing, the titanium surface became dark blue.

The complex dielectric permittivity functions as well as the refractive indices of the samples were registered by means of the spectral ellipsometer Auto SE (Horiba, Japan) in visible wavelength range at the standard (70°) angle of incidence. All spectral measurements were performed with the use of DeltaPsi software, which allowed optical spectra obtaining in 30 points on the 0.0225 mm$^2$ surface followed by averaging procedure. The relative experimental error of all the optical measurements was 4%.

The electronic images (SEM-images) of titanium surfaces with different roughness were obtained using electronic microscope Zeiss Cross Beam 540.

3. RESULTS AND DISCUSSION

The structural characteristics of the titanium surfaces before and after anodizing are presented in Figures 1 and 2, respectively.

![Figure 1. SEM-image of the titanium surface before anodizing.](image1)

![Figure 2. SEM-image of the titanium surface after anodizing.](image2)
Figure 1 illustrates SEM-image of the titanium surface before anodizing. As it can be seen from the figure, the sample has granular structure, which is characteristic of metal.

The SEM-image of the titanium surface after anodizing at 30 V is shown on the Figure 2. The structure of the surface, as it can be seen from the figure, changed greatly: it became more rough and loose. Pores can be observed clearly on the surface layer of the titanium with oxide film of the mean radius of 50 nm.

In the second series of the experiment, the titanium surface with the different structure complex dielectric permittivity functions spectra have been obtained.

The titanium surface complex dielectric permittivity functions are presented in Figures 3 and 4 for the samples before and after anodizing, respectively.

Figure 3. Complex dielectric permittivity of the titanium surface before anodizing (blue line – real part; red line – imaginary part).

Figure 4. Complex dielectric permittivity of the titanium surface after anodizing (blue line – real part; red line – imaginary part).
Figure 3 shows that for the sample before anodizing, the real part of the complex dielectric permittivity has negative values through the whole visible and near IR wavelength range while the imaginary part is positive and increases with the wavelength. Such a behavior of the curves is characteristic of a smooth mirror-like titanium surface [10] and can be described exclusively by the Drude free electron oscillation model in the visible wavelength range. The real and imaginary parts of the complex dielectric permittivity function magnitudes are within the ranges \(-2 < \text{Re}\{\varepsilon(\lambda)\} < -1\) and \(7 < \text{Im}\{\varepsilon(\lambda)\} < 13\), respectively.

It should be mentioned that the imaginary part of the complex dielectric permittivity function is associated with light absorption by the media and indicates the surface plasmon oscillations at certain frequencies [10, 12]. It should also be said that such oscillations cannot be generated on a mirror-like metallic surfaces [10], which is proved by \(\text{Im}\{\varepsilon(\lambda)\}\) curve behavior: \(\text{Im}\{\varepsilon(\lambda)\}\) does not contain maxima though the whole investigated wavelength range.

Let us consider the behavior of the complex dielectric permittivity for anodized at 30 V titanium surface.

It can be seen from Figure 4, the spectrum of complex dielectric permittivity has a maximum; the positive values of \(\text{Re}\{\varepsilon(\lambda)\}\) are related to the 500 \(\div\) 650 nm wavelength range. Within this interval, \(\text{Im}\{\varepsilon(\lambda)\}\) is negative for the wavelengths from 510 to 640 nm.

Surface plasmon oscillations resonance frequency for metals corresponds to the wavelength range satisfying the following condition:

\[
\text{Re}\{\varepsilon(\lambda)\}\cdot\text{Im}\{\varepsilon(\lambda)\} < 0.
\]

Since the negative real part of the complex dielectric permittivity is known to correspond to mirror-like metallic surface [13], we now proceed with consideration of positive \(\text{Re}\{\varepsilon(\lambda)\}\) and negative \(\text{Im}\{\varepsilon(\lambda)\}\) values.

Thus, in the 510 \(<\lambda\) < 640 nm wavelength range, surface plasmons can be generated on the titanium rough surface – TiO\(_2\) oxide film. It becomes possible to fabricate a rough titanium surface with a given geometric structure and optical properties.

In the third series of the experiment, we studied the spectra of the rough titanium surface refractive index.

Figure 5 illustrates the spectrum of the rough titanium surface with the oxide film refractive index.

\[
\text{Figure 5. Spectrum of the rough titanium surface with the oxide film refractive index.}
\]

It can be seen from the figure that the spectrum \(n(\lambda)\) has a local peak (minimum) at \(\lambda \approx 580\) nm. The real part of the complex dielectric permittivity has a maximum at this wavelength (see Figure 4).
It should also be mentioned that there are negative values of $n$ occurring in a wide wavelength range (500 \(\div\) 730 nm), which corresponds to the surface generation wavelength interval (see Figure 4) [14, 15]. Thus, we experimentally created the titanium rough surfaces – titanium oxide film interfaces with negative refractive indices in the visible wavelength range.

4. CONCLUSION

In the present work, it was shown that a rough titanium surface covered with a thin island titanium oxide film can be considered as a media with possible generation of the surface plasmons in the visible wavelength range. $\lambda = 600$ nm appeared to be a wavelength, at which the incident electromagnetic radiation is totally absorbed by the surface. It was also found that the negative values of the titanium rough surface – titanium oxide film interface are due to the surface plasmon oscillations generation. The latter allows studying novel media with given optical properties in order to be used as nanosensors and nanoelectronic devices.

The results obtained within this work can be used to create porous metamaterials as well as in quantum electronics for reflected and refracted radiation properties change by altering the surface structure of the sample.

5. ACKNOWLEDGEMENTS

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