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Polarized plasmon resonance spectra of electrochemically modified titanium surfaces with gold nanoparticles

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Abstract

In this paper, the plasmon resonance on electrochemically modified titanium surfaces synthesized by anodic dissolution method has been studied in the presence with gold ablative nanoparticles. The permittivity functions and reflection coefficients of p- and s-polarized light spectra on the titanium oxide surface of various modification (roughness) have been analyzed. Spectral features of the negative refractive index in the area of surface plasmon generation on the rough titanium-oxide film interface have been also presented in this paper.

1. Introduction

Currently, titanium-based materials are widely used in the field of medicine [1, 2], photovoltaics, and optoelectronics [3–7] due to its unique physical and chemical properties. Of particular practical interest are titanium oxide nanoparticles of various shapes (nanotubes, nanorods, etc) synthesized by electrochemical anodizing method [8–10].

As shown in our previous papers [11, 12] the titanium rough surface with gold nanoparticles could create a Surface-Enhanced Raman Scattering (SERS) and enhance the platelet detection signal, so it makes anodized Ti surface a good potential application in practical medicine. The nature of this amplification is not fully understood due to certain difficulties associated with the optical properties of surfaces and nanostructures. For example the generation of surface plasmon polaritons by an electromagnetic field [13] that occur only on a rough metal surface makes an additional contribution not only to the spectral composition of the functions ε(λ), but also changes the optical characteristics of the reflection coefficients of p- and s-polarized radiation and the refractive index. In the presence of a nanometer-scale oxide surface layer, the spectrum of ε(λ) for surface plasmons also changes [14–17].

Doping the oxide layer with nanoparticles can lead to spectral shifts and some changes in the shape of the spectrum, which allows to control the position of the local plasmon resonance, it’s enhancement or attenuation. Thus, the synthesis and application of modified titanium surfaces for nanooptics expands the range of plasmon resonance applications in various fields: photovoltaics, optoelectronics, and biosensors [3, 8–20].

Therefore, the purpose of this work is to study the optical and dielectric properties of the nanostructured anodized titanium surface with gold nanoparticles: the spectral composition of the real and imaginary parts of the permittivity functions, the reflection polarization and refractive index spectra of the anodized titanium surface. It was also of great interest to determine the efficiency of generating plasmons on such surfaces under changing the roughness of the surface structure conditions.

2. Materials and methods

Anodizing of titanium plates was performed according to the electrochemical method in a potentiostatic mode at electrode voltages of 20 and 30 V [11]. On the rough anodized Ti surface (U = 30 V) gold nanoparticles (NPs)
prepared by femtosecond laser ablation method [21] was deposited. The concentration of gold nanoparticles in hydrosol solution after ablation process was $C = 10^{-10}$ M.

The average hydrodynamic radius of the obtained ablative nanoparticles was determined by dynamic scattering method at the photon correlation spectroscopy set (Photocor-Complex, Belarus). The irradiation wavelength was $\lambda = 452$ nm.

The polarized plasmon reflection coefficients and the dielectric permittivity functions were measured by means of Auto SE spectral ellipsometer (Horiba, Japan) in the visible wavelength range. Mathematical calculating of the spectra was carried out using DeltaPsi software for the ellipsometer, which allowed to record an optical spectra in 120 points on the 2500 mkm$^2$ place with following averaging. The thickness of the oxide films was also determined by ellipsometric methods [22]. The reflection spectra of unpolarized light were measured with using a spectrophotometer Shimadzu (Japan). The surface structure of modified titanium surfaces was investigated by means of Zeiss Cross Beam-540 (FIB-SEM) electron microscope operating at 5 kV.

3. Results and discussion

In the first series of experiments, the anodized structures of titanium plates were studied on a scanning electron microscope after various anodizing modes and in the presence of Au nanoparticles. Figure 1 shows SEM images of the investigated Ti modified surfaces.

Figure 1(a) demonstrates a granular structure of the Ti surface, which has not been exposed to anodizing process. At $U = 20$ V the surface structure has visible roughness and pores (diameter of up to 50 nm). A further increase in the voltage up to $U = 30$ V during anodizing resulted in significant changes in the titanium samples porosity (figure 1(c)). It can be noticed the presence of different heights of rough surface elements and the surface becomes loose. The figure 1(d) shows that spherical Au NPs are rather well adsorbed on this surface ($U = 30$ V), forming strong clusters with elements of roughness anodized Ti surface. According to the size distribution function shown in the inset in figure 1(d), the average hydrodynamic radius of Au NPs is $R = 28$ nm. Also, a small number of larger nanoparticles with a radius of $\sim 70$ nm can be seen on the SEM image of figure 1(d).

Thus, the obtained images of the modified anodized titanium surfaces indicate differences in the roughness of the surface structure, but roughness parameters estimation can be made only by means of other techniques.
The average thickness values of the TiO$_2$ film were determined by ellipsometry method by means of theoretical simulation of the reflection coefficient. It should be said that all optical spectra were measured at 120 points and did not change during the entire measurement. Thus, the obtained TiO$_2$ thickness values at voltages of 20 and 30 V are $\sim$30 nm and $\sim$50 nm, respectively.

The dielectric permittivity functions of Ti surfaces are presented on figure 2. As can be seen from figure 2(a) for pure Ti surface (before anodizing process) the Re($\varepsilon$) and Im($\varepsilon$) functions have a different signs in all visible region. While considering the spectra of Re($\varepsilon$) and Im($\varepsilon$) permittivity (figures 2(b), (c)) it can be noticed that the spectra have extreme values due to the presence of surface roughness as a result of titanium anodizing. According to the theory of plasmon interactions in the medium, the resonant frequency of vibrations for metals corresponds to the region where the condition Re($\varepsilon(\lambda)$)*Im($\varepsilon(\lambda)$) $<$ 0 is satisfied [23]. The negative real component is known to correspond to a mirror-like metal surface [24], thus, further, when analyzing the $\varepsilon(\lambda)$ functions, we will consider Re($\varepsilon(\lambda)$) $>$ 0 and Im($\varepsilon(\lambda)$) $<$ 0, assuming that the existence of surface plasmons in these ranges is possible due to a free electrons fluctuations bound by Coulomb interaction forces. The spectral regions of the functions Re($\varepsilon$) and imaginary Im($\varepsilon$) of the anodized surfaces where the generation of surface plasmons is observed will be shaded in the figures.

Figure 2(b) illustrates a maximum in the Re($\varepsilon$) spectrum. The region of positive values for Re($\varepsilon$) is located in the wavelengths range of 500 – 650 nm. The Im($\varepsilon$) has a negative sign within a range of 550 to 650 nm. Consequently, in the range of 550 $<$ $\lambda$ $<$ 650 nm (figure 2(b)), it is possible to generate surface plasmons on the interface rough titanium—oxide film TiO$_2$. Figure 2(c) shows that the $\varepsilon(\lambda)$ functions have one peak at a $\lambda$ = 620 nm and at a $\lambda$ = 570 nm for the Re($\varepsilon$) and Im($\varepsilon$) respectively. In the shaded area, the components of the $\varepsilon(\lambda)$ function have different signs. As can be seen from this figure, the surface plasmon generation possible wavelengths are located in the red region of the optical spectrum. Thus, with an increasing voltage in the anodizing process, the structural changes in the TiO$_2$ morphological properties films (figure 1) occur resulting in electro–optical features change along with spectral changes in the surface plasmons generation.

Since it was shown in the cited literature resources that anodizing and roughness are interdependent concepts, the presence of spectral regions of surface plasmon generation reflects the degree of surface roughness,
which is difficult to quantify [25]. Figure 2(c) shows that the narrow spectral ranges (~60 nm) of plasmon generation are red-shifted (640 < λ < 700 nm).

The regions of surface plasmon generation for Ti anodized surface with Au nanoparticles (figure 2(d)) are 450 < λ < 550 nm and 640 < λ < 720 nm. It can be noticed that there is a spectral plasmons overlap in red region (figures 2(c), (d)). For this purpose, we will consider the polarization features of anodized titanium with various electrochemical anodizing.

The propagation of surface plasmons on anodized titanium surfaces has different effects on the polarization characteristics of the reflected light from the metal-oxide surface interface, which is a thin dielectric-metal film with chaotic roughness, internal dimension and topological effects. The presence of ‘gold’ plasmons makes an additional contribution to the spectral composition Rp and Rs polarized light.

Figures 3(a), (b) show the reflection coefficients Rp and Rs spectra of anodized titanium at 20 and 30 V. The presented spectral polarization dependences of the reflection coefficients are almost identical in shape and value. This behavior of the reflection coefficients spectral dependences of polarized radiation from rough Ti surfaces may be related to the existence of an isotropic type of radiation reflection from the studied surfaces [26, 27] because the roughness is stochastic. In this case, the reflection spectra minima are red-shifted with an increase in the anodizing voltage. It should be noticed that the position of the reflection coefficients minimum is related to a sharp increase in the electromagnetic field at the metal-dielectric interface associated with the appearance of surface plasmons. These minima coincide with the spectral positions intensity of surface plasmon generation peaks at the wavelengths of 570 (U = 20 V) and 620 – 650 nm (U = 30 V) (figures 3(b), (d)) where the maximum absorption occurs. The reflection spectra for the surface with Au NPs (figure 3(c)) has a plasmons absorption resonance at wavelength of 550 nm due to electron density oscillation of gold nanoparticles. In the red region of wavelengths it can be noticed a change in the shape of the spectrum, Rp and Rs coefficient are also increased.

These results confirm the previous arguments about the existence of plasmon oscillations in wavelengths regions with Re(ε) > 0 and Im(ε) < 0.

Figure 3(d) demonstrates the simulation processes of absorption polarized light on the anodized Ti surface obtained at anodizing voltage of 30 V. The Rs spectrum was calculated using the Brodsky model [25]:

\[ R^I_S = |r_\text{opt}|^2, \]
function that depends on the optical microscopic parameters of the surface. The value

\[
\eta = \frac{\Delta R_p^{ps}}{R_p}
\]

is 1.5.

Thus, when obtaining the Rs coefficient for the Ti surface (U = 30 V) (figure 3(d)), the critical points of the maxima and minima of the reflection coefficients on the polarization dependence curves were determined.

We can estimate how many times the conversion of incident energy into plasmon energy is more efficient on surfaces obtained at U = 20 V, 30 V and on the surface with Au NPs. The efficiency incident energy converting into plasmon energy is related to the roughness and optical functions by the following equation [25]:

\[
\eta = \frac{\Delta R_p^{ps}}{R_p} = \xi^2a^2f(\varepsilon_1, \varepsilon_2, \theta, k),
\]

where \(\xi\) is the surface roughness; \(a\) is the standard average distance between irregularities; \(f(\omega_0, \varepsilon_1, \varepsilon_2, \theta, k)\) is a function that depends on the optical microscopic parameters of the surface. The value \(\Delta R_p^{ps}/R_p\) shows the fraction of incident p-polarized light converted into the surface plasmons.

The \(\eta_1/\eta_2\) ratio characterizes the influence of the surface roughness degree on the energy conversion:

\[
\eta_1/\eta_2 = (\xi_1a_1)^2/(\xi_2a_2)^2
\]

Considering the anodized surfaces obtained at a voltage of 20 and 30 V, it can be found \(\eta_1/\eta_2 = 3.2\).

For the anodized surface obtained at a voltage of 30 V and this surface with Au NPs for red region of the spectral range the ratio \(\eta_1/\eta_2\) is 1.5.

Let us consider how the refractive index of rough investigated titanium surfaces (figures 1(b)–(d)) changes, on which plasmon resonance occurs. Figure 3(e) (inset) shows the spectra of the refractive index of titanium surfaces with different surface roughness degrees in the presence of an oxide film.

As can be seen from the figure 3(e) unpolarized reflection spectra are quite wide due to the porosity and combined composition of the surface (Ti/TiO2/Au NPs). This spectral width may also be due to the presence of overlapping plasmon spectra (occurring at the Ti/TiO2 interface and the plasmon resonance of gold nanoparticles), which can only be resolved by considering reflected polarized light. That’s why the study of Rp and Rs polarized components was of particular interest in this paper.

Figure 3(e) (inset) shows the presence of a minimum in n(\(\lambda\)) spectrum, which is red-shifted with the titanium surface roughness increase. The obtained spectral changes can be considered by detail in conjunction with the results of the permittivity and reflection spectra of the studied surfaces. Thus, the region of surface plasmon generation according to the previous dielectric permittivity spectra (figure 2, figures 3(a)–(c)) corresponds to the wavelengths regions 500 < \(\lambda\) < 725, 540 < \(\lambda\) < 785, \(\lambda\) > 753 nm where the refractive index values are negative (figure 3(e) inset). Consequently, the existence of plasmon oscillations on rough surfaces in these regions causes the presence of negative values in the n(\(\lambda\)) spectrum, and the comparison of the permittivity and refractive index graphs for these surfaces makes the expression \(n = -(\varepsilon_1)_{1/2}\) to take place.

According to the recent papers, there are several research groups that consider the processes metasurfaces synthesis along with the methods for modeling the interaction of electromagnetic radiation with surfaces with a negative refractive index [28–32].

Thus, a large concentration of charges accumulating on the roughness elements and in the pores formed during anodizing process causes a strong absorption of electromagnetic radiation by the surface in the negative region of the refractive index function depending on the wavelength.

4. Conclusions

In summary, it was shown that on the rough titanium surface in the presence of a thin TiO2 oxide film, it is possible to generate surface plasmon oscillations in the visible region of the spectrum. The plasmon resonance is red-shifted with the anodizing voltage increase. It was found that the region of existence of a negative refractive index is due to the generation of plasmon oscillations on rough titanium surface –TiO2 oxide film interface. It was established that the fraction of incident energy conversion into the SP energy for a rougher surface is 3.2 times higher. Also the efficiency of energy conversion to surface plasmons in the presence of Au nanoparticles is 1.5 times higher than on the anodized Ti surface without NPs. The occurrence of surface
plasmon vibrations at the boundary of the rough surface of titanium with the oxide film causes a change in the sign of the refractive index. The appearance of negative values in the spectrum of n(λ) allows to obtain new information about the interaction of radiation with the material at certain frequencies, which is an important aspect in the creation of nanodevices and nanosensors.

The results obtained in this paper can be used in the creation of porous metamaterials and quantum electronics to change the optical properties of reflected and absorbed radiation by changing the surface roughness geometry.

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