The use of plasmon resonance spectroscopy to analyze the parameters of thin layers

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Abstract. The paper presents the results of calculating the angular spectra of ellipsometric parameters and ellipse parameters upon reflection of right-polarized light onto the Kretchman layered system under conditions of excitation of surface plasmons at the boundary of the silver metal layer. It is shown that the studied parameters turn out to be very sensitive when a film of the material under study is placed in a layered system. The conditions are found under which a change in the nature of the polarization of the reflected wave occurs - from the right circular wave of the incident wave to the left elliptical in reflected light. Thus, the use of circular polarization and ellipsometry in plasmon resonance spectroscopy expands the possibilities of this method, in which only the energy reflection coefficient of p-polarized light is studied.

1. Introduction
The method of spectroscopy of Attenuated total reflection is widely used to study the properties of various material media. The authors of [1-3] considered the joint Attenuated total reflection method together with infrared spectroscopy with Fourier transform. In [1], this method is used for medical diagnostics, in [2] for studying diseases in plants, and in [3] for studying particle adsorption on catalysts.

In [4], the deposition of platinum particles on titanium oxide was studied. In [5], the method is used to study the vibrational modes of a number of biological and chemical materials. In [6], ATR spectroscopy was expanded to nonlinear optical phenomena; in particular, Raman scattering was considered to determine the thickness of thin films.

The use of light of general elliptical polarization makes it possible to obtain more detailed information about the object under study. In [7], general polarization light was used for polarimetric measurements of homogeneous samples. In [8], the polarization of terahertz radiation of a femtosecond laser filament was analyzed. In [9], elliptical polarization light is used to encrypt images. In [10], a polarization state was analyzed for a CO2 laser, and in [11] elliptically polarized light was used to study the linear and nonlinear susceptibilities of a graphene nanostructure.

Recently, together with ATR spectroscopy of surface plasmon resonance (SPR) with excitation of surface polaritons to the boundaries of the structure under study has become widespread. In [12], a fiberoptic sensor based on surface plasmon resonance was considered. In [13], a measurement was made of the plasma frequency of an SPR-based semiconductor film. In [14], a modulator for the terahertz wave is presented, formed by the metal – insulator – metal structure. In [15], light transmission through a terahertz metamaterial in the surface plasmon resonance region was studied. In [16-17] with the participation of the author of this article, the possibility of excitation of surface polaritons and plasmons with a negative group velocity was investigated.
1.1. Formulation of the problem
A plane harmonic electromagnetic wave of circular polarization is incident at an angle on the layered system shown in figure 1. The wave parameters are selected from the condition for the excitation of a surface plasmon at the boundary of a 2-3 layered system. The angle of incidence $\theta_0$ varies from 0 to 90 degrees. The calculation was carried out for two versions of the layered system. In the first layer 1, 2 and 4 are presented, in the second - the entire system of layers is completely. In this case, the object of study is material 3, as an example for which we consider a layer of gasoline with a refractive index of $n_2 = 1.5$. It is necessary to compare the angular dependence of the modulus of the ellipsometry parameter of reflected light for two cases. In addition, the angular spectrum of the parameter describing the nature of the ellipse of polarization of the reflected wave will be analyzed.

![Figure 1. Kretchman layered system: 1 — dielectric prism, 2 — metal layer, 3 — test layer, 3 — air.](image)

1.2. Theoretical consideration
The ellipsometric parameters of the reflected light are determined from the condition

$$\hat{\rho} = \rho \cdot e^{i\Delta} = \frac{R_p}{R_s},$$

(1)

where $R_p, R_s$ are the amplitude reflection coefficients for p - and s - polarizations, respectively.

![Figure 2. Polarization ellipse.](image)
The elliptical polarization of a plane harmonic electromagnetic wave is described by the parameters $a$ - major axis, $b$ - smaller axis, $\alpha$ - angle of inclination of the major axis of the ellipse to the x axis. The calculated parameter is the angle $TH$, which is determined from the condition

$$\tan TH = \pm \frac{b}{a}. \quad (2)$$

The sign in this formula describes the nature of the elliptical polarization - plus corresponds to the right polarization, and minus corresponds to the left.

1.3. The Calculation Method

The calculation of the layered system was carried out by the method of characteristic matrices. For s- and p-polarizations included in the general elliptical polarization, this method establishes a relationship between the continuous components of the electromagnetic fields at the boundaries $z = 0$ and $z = dn$ of the layered system

$$\vec{Q}(z = 0) = \vec{M} \cdot \vec{Q}(z = dn).$$

In the case of s-polarization, the elements of the column vector $\vec{Q}$ are the fields $E_y$ and $H_z$ for p-polarization - $H_y$ and $E_x$. For the two variants of layered systems described above, their characteristic matrices were found and with their help ellipsometric parameters were calculated, as well as polarization ellipse parameters $a$, $b$, $TH$.

Surface plasmons are waves propagating along the interface of media, one of which is surface-active, having a negative real part of the dielectric constant. The electromagnetic field of a surface plasmon is described by a function exponentially decaying at both interfaces

$$H_y = H_0 \exp(-\kappa z) \exp(ik_{\parallel}x - i\omega t),$$

where $\kappa$ is the wave attenuation parameter along the z axis, $k_{\parallel}$ is the wave number describing the wave propagation along the x axis.

The dispersion equation for a surface plasmon at the boundary of two media is given by the equation

$$k_{\parallel}^2 = \frac{\omega^2}{c^2} \cdot \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2},$$

where $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of the contacting media.

2. Calculation results

The calculation results are presented in figures 3-5. As a conductor, we chose silver, whose complex dielectric constant at the wavelength $\lambda = 633$ nm has a negative real part $\varepsilon_1 = -18.2 + 0.5i$. Calculation parameters: silver layer thickness $d = 0.05 \mu$, gasoline layer thickness $da = 0.05 \mu$, gasoline refractive index $na = 1.5$

2.1. Modulus of the ellipsometric parameter

Figure 3 shows the angular spectra of the modulus of the ellipsometric parameter of the reflected wave for two schemes of layered systems. The first curve $mo$ refers to the absence of the studied layer. A sharp minimum characterizes plasmon resonance at the boundary of the silver layer. The second curve $moA$ describes the angular spectrum of the layered system taking into account the layer. Comparing the nature of the dependences, we see that the minimum in the second case shifts relative to the initial minimum, which is the main result of plasmon resonance spectroscopy. Parameters
Figure 3. Angular spectra of the modulus of the ellipsometric parameter of the reflected wave.

2.2. Angular spectrum of the ellipse parameter $TH$
Of particular interest is the result shown in figure 4, which shows the angular spectrum of the ellipse parameter $TH$, which describes the ratio of the semiaxes of the ellipse. It can be seen from the figure that the reflected wave has an elliptical polarization with a varying semiaxis ratio with a change in the angle of incidence $\theta_0$. In this case, there are regions of incidence angles in which the right circular polarization of the incident radiation turns into the left elliptical upon reflection. Such regions of a change in the nature of polarization carry additional information and extend the traditional method of plasmon resonance spectroscopy to the case of circularly polarized waves.

Figure 4. Angular spectra of the modulus of the ellipsometric parameter of the reflected wave.
2.3. Position of the minimum angle in the angular spectrum of the ellipsometry parameter module

Figure 5 shows the dependence of the position of the minimum angle in the angular spectrum of the ellipsometry parameter module on the refractive index of the layer under study. It follows from this figure that the method is very sensitive to a change in the refractive index and can be used for precision measurements of this parameter for a wide class of substances.

![Figure 5](image-url)

**Figure 5.** The minimum modulus of the ellipsometric parameter as a function of the refractive index $n_a$ of the layer.

3. Conclusion

This paper presents the results of calculating the angular spectra of ellipsometric parameters and ellipse parameters upon reflection of right-polarized light onto the Kretchman layered system under conditions of excitation of surface plasmons at the boundary of the silver metal layer. It is shown that the studied parameters turn out to be very sensitive when a film of the material under study is placed in a layered system.

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