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Optical properties of thin gold films

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Abstract. Results of studing optical constants of thin gold films are given. The values of refraction and extinction coefficients (n, æ, respectively) are calculated from reflection and transmission spectra accordingly to traditional formulae, and using new theory as well. The comparison of the results obtained by both means was held, and possible causes of divergences were considered.

Keywords: thin films, refraction coefficient, reflection coefficient, atomic-force microscopy.

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1. Introduction

For many years calculation of the optical constants of thin films has been based on using correlations that consider multiple reflection and interference; and the intensities of light beam reflected and transmitted by a thin layer appear to be experimentally determined. The formulae of the latter ones comprise Fresnel's coefficients of reflection and transmission of air (vacuum) – thin layer and thin layer – substrate interfaces.

In a case of the absorbing media, the refraction coefficient is usually written in a complex form, that is transition from transparent to absorbing medium is postulated by the formal substitution $\tilde{n} \to n \pm i$æ. Perhaps the very substitution leads to the results devoid any physical meaning. For example, with the reducing thickness of thin gold films [1-3] (Fig. 1) and atomic semiconductors [4-6] to zero value, the refraction coefficient grows unlimitedly although it must tend to unity. Such a monotonous thickness dependence appears to be more doubtful, while in a very wide interval of thickness, used in the paper cited, at least one resonance maximum on $n = f(d)$ curve must take place. Calculations made according to the traditional formulae do not give such a maximum.

While researching optical properties of bulk samples and thick films of metals, including precious ones, one obtains n values in wide regions of a spectrum. Data of papers [8-10] are given as an examples in Fig. 2. In the first two references, opaque layers of gold are used, obtained by vacuum deposition on glass substrates for measurements of the optical constants, while in [10] – monocrystals of gold are investigated.

In the spectral region 0.5-2.5 μm the authors of the mentioned works obtained $n < 1$ value. n and æ divergence of different authors can be explained by different conditions of sample preparation, as well as by their surface state and errors of measurements.

In the infrared region ($\lambda = 1 \div 12$ μm) of spectrum these gold films are investigated in [11-13]. Their results are given in Fig. 3. In the 1-2.5 μm region the refraction index appeared to be less than unity.

Surprising is not only the existence of inequality $n < 1$. It is even harder to imagine why it is characteristic for the wide spectral regions, while the minimal value of n appears in a comparatively small interval of frequencies, where maxima of absorption bands are situated, caused by band-to-band transitions or oscillation of the crystal lattice, that is in the region of anomalous dispersion.

A group velocity, which the energy is carried with, is known as

$$V_{gr} = \frac{c}{n - \dfrac{dn}{d\lambda} \cdot \lambda} \tag{1}$$

where c is the velocity of light in a vacuum. As a phase velocity $V_{ph} = c/n$, then at the frequencies, where $dn/d\lambda$ sign changes, that is at the extremum points of a dispersion curve, which limit the region of anomalous dispersion, $dn/d\lambda = 0$, so instead of (1) we get:

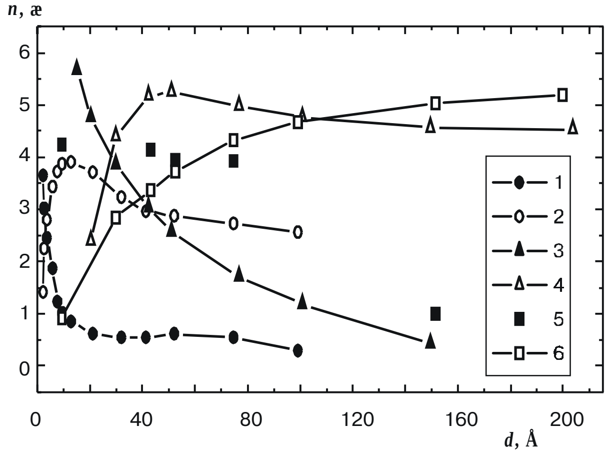

Fig. 1. Dependences of optical constants of gold on a layer thickness for $\lambda = 7000$ Å
1,2 – n and æ [3]
3,4 – n and æ [2]
5,6 – n and æ [1]

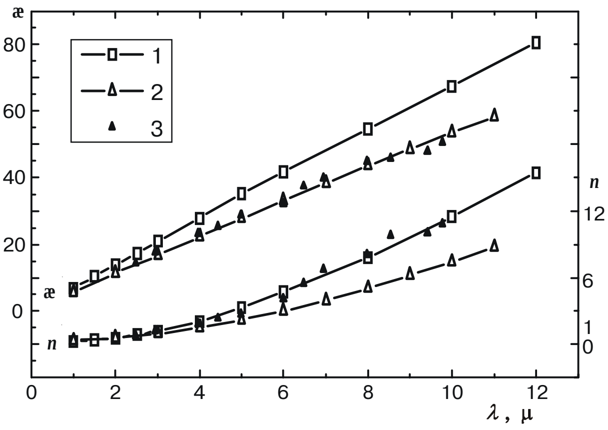

Fig. 3. Optical constants n and æ of bulk gold samples in the infrared spectral region. 1, 2, 3 – data of [11], [12], [13], respectively.

$$V_{gr} = \frac{c}{n} = V_{ph} > c \tag{2}$$

because $n < 1$. This result contradicts the special theory of relativity, in accordance with which group velocity can not exceed the velocity of light in a vacuum.

To our mind the above-mentioned examples are enough to reason a search for new approaches while solving the problems of optics of thin layers and solid states in spectral regions of intense light absorption.

T.A. Kudykina made first steps in this direction [14]. Using Maxwell's boundary conditions, she got analogs of Fresnel's formulae without applying $\tilde{n} \rightarrow n \pm i$æ substitution. By calculations according to these formulae obtained earlier [4-6], of the experimental curves of transmission and reflection of Te, Se, Ge thin films, the thickness dependencies of optical constants n and æ [15] were determined. They differ principally from dependencies received earlier: each curve has a resonance maximum, and with thickness of a layer decreasing to zero, n, as it was expected, tends to unity.

Spectral dependencies of optical constants of thick films of gold are represented in Fig. 4. They were calculated accordingly to experimental data [8] using formulae of T.A. Kudykina. In the whole range of the waveslengths, refraction coefficient, calculated according to these formulae, exceeds unity.

The above-mentioned examples show suitability of new formulae for existing optical constants of solid states in spectral areas of strong absorption. However, as it will be shown in further discussion of some results, these formulae do not withdraw the existing difficulties. Moreover, there occur some questions, which have no simple answers.

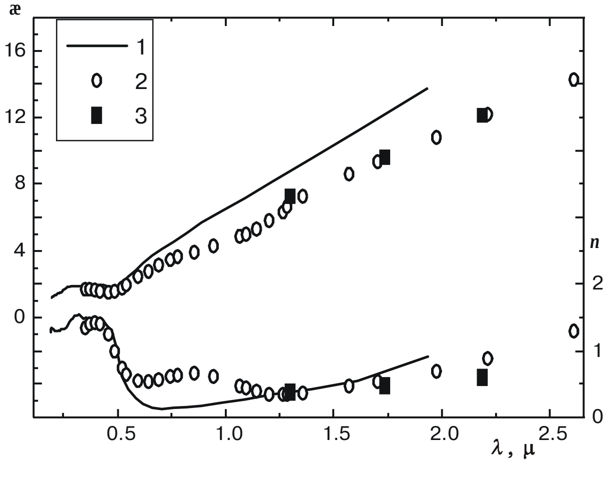

Fig. 2. Optical constants n and æ of bulk gold samples.
1, 2, 3 – data of [8], [9], [10], respectively.

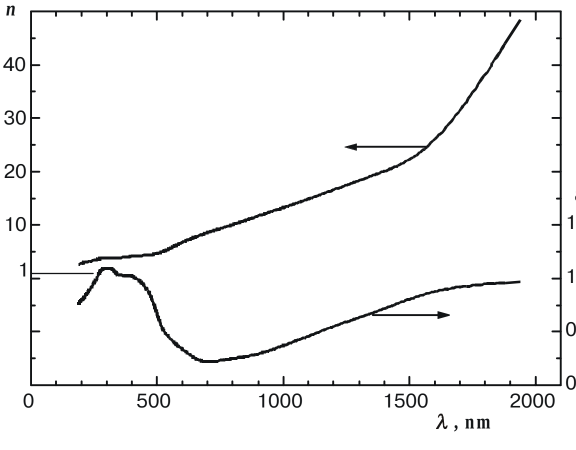

Fig. 4. Optical constants of gold, calculated using formulae of [14] according to experimental data of [8].

2. Experiments and their discussion

Samples of thin layers with different thickness were produced by thermal evaporation of gold in vacuum ~10^{-5} Torr on quartz substrates at room temperature. The purity of initial material was not worse than 99.99%. The deposition rate was 2-10 Å/c. In the process of deposition the thickness of films was controlled using a quartz resonator, and right after deposition was measured by atomic-force microscope.

In Fig. 5 the structure and distribution of irregularities of a gold film, obtained using the same microscope, are represented. The image is identical to photopictures, obtained by an electronic microscope [16]. At a first glance the film seems to be island-like, but measurements show that cavities, met along the drawn line, make up less than 30% from the film's thickness. Therefore, it can be considered to have quite a flat surface, because the sizes of inequalities are much smaller than λ.

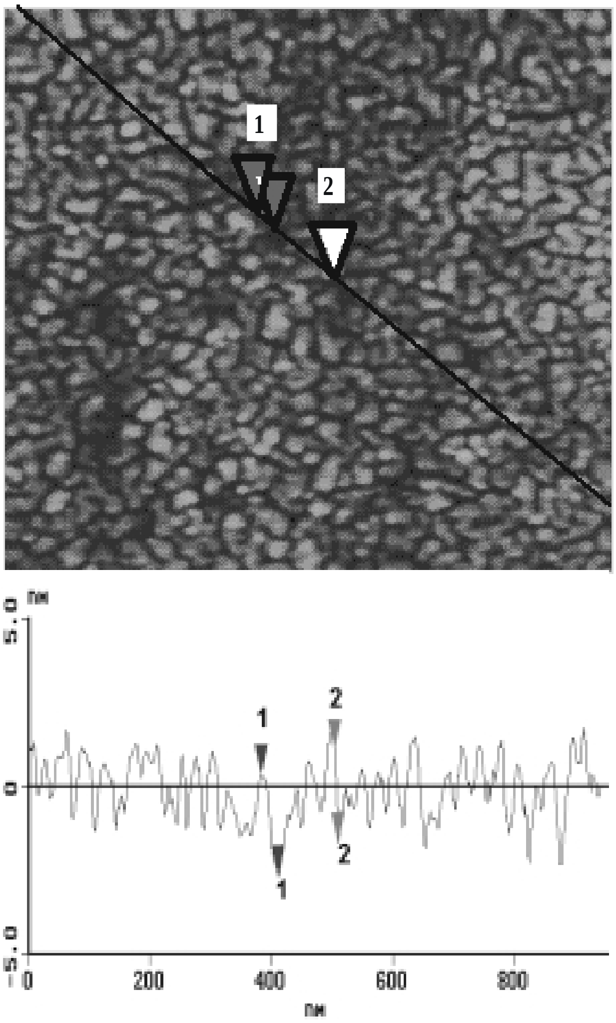

Fig. 5. An image of a part of a gold film with dimensions 720nm×720 nm and the effective thickness of 85Å, obtained by using an atomic-force microscope.

For a better visible relief perception, a photograph of a film in axonometric projection is represented in Fig. 6a in a somewhat stretched scale along the vertical line. Fig. 6b illustrates heterogeneity of a film in its thickness, which can be partly a result of imperfections of the substrates' surface: a mean square value of its inequalities made up 30Å.

Measurements showed that average thickness in some regions of a film with the area ~10 μm^2 changed for pattern N1 within 83-87Å, N2 – 121-126Å, N3 – 129-136Å, N4 – 180-188 Å. For an effective thickness its average value is taken.

With the thickness increase the nature of surface remains the same, but sharp juts become somewhat thicker, and deep cavities become filled up. A scanning held 5 months later showed no morphological changes in all the patterns.

Constants *n* and æ were calculated in the spectral range 4000-8000 Å. Reflection *R* and transmition *T* coefficients of the film-substrate system were measured using a set based on a monochromator MDR-23. Accuracy of measurements was 1%.

The optical constants of thin gold layers were calculated by expressions in which interference is taken into account:

$$R = \frac{r_{12}^2 + r_{23}^2 \exp(-2\alpha d) - 2r_{12}r_{23}\exp(-\alpha d)\cos\psi}{1 + r_{12}^2 r_{23}^2 \exp(-2\alpha d) - 2r_{12}r_{23}\exp(-\alpha d)\cos\psi} \qquad (3)$$

$$T = \frac{T_{12}T_{23}\exp(-\alpha d)}{1 + r_{12}^2 r_{23}^2 \exp(-2\alpha d) - 2r_{12}r_{23}\exp(-\alpha d)\cos\psi} \qquad (4)$$

$$\alpha = \frac{4\pi\, æ_2}{\lambda} \qquad (5)$$

$$\psi = \frac{4\pi}{\lambda} n_2 d \qquad (6)$$

In contrast to the old theory [7], the amplitude factors of reflection and transmission of certain boundaries in the new theory [14] do not contain values of absorption for normal incidence of a light beam; however, for the inclined ones, falling on the boundary of these two media, those factors are the functions of both refraction coefficient *n* of an absorbing layer and its extinction coefficient æ. The fact of a normal incidence having some anomalous properties in comparison with a case of inclined incidence arouses surprise. But we must follow the theory, so we show the above-mentioned amplitude factors in accordance with its demands.

So we have:

$$r_{12} = \frac{n_2 - n_1}{n_2 + n_1}; \quad r_{23} = \frac{n_3 - n_2}{n_3 + n_2} \qquad (7)$$

$$t_{12} = \frac{2n_1}{n_2 + n_1}; \quad t_{23} = \frac{2n_2}{n_3 + n_2} \qquad (8)$$

$$t_{21} = \frac{2n_2}{n_1 + n_2}; \quad t_{32} = \frac{2n_3}{n_2 + n_3} \qquad (9)$$

Here, index 1 means air, 2 – film, 3 – substrate.

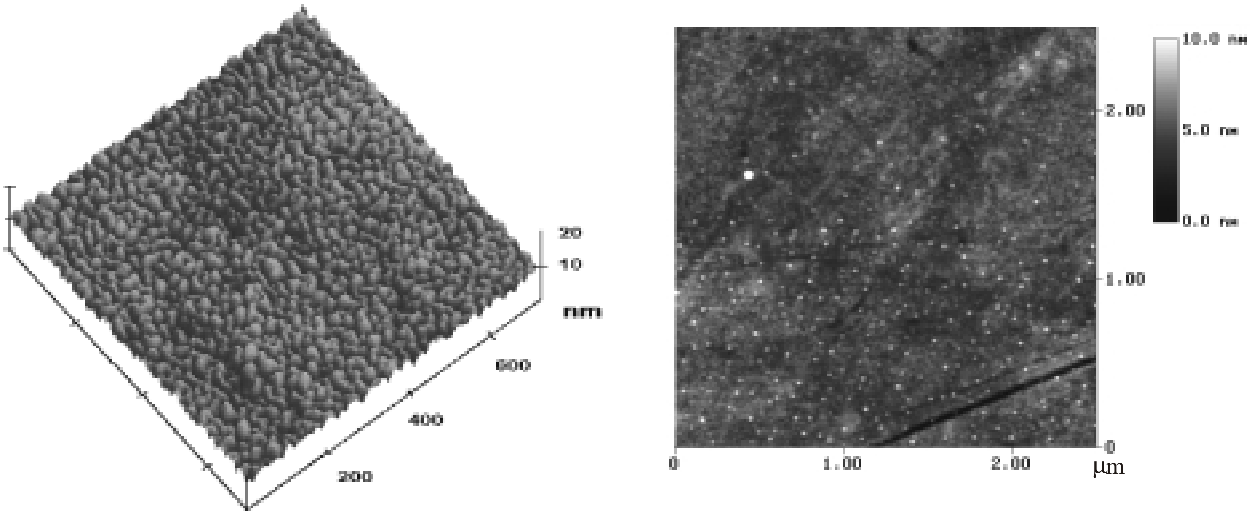

Fig. 6. Axonometric image of a gold film, obtained by using an atomic-force microscope.

Having made the change $Z = \exp(-\alpha d)$, instead of (3), (4) we get quadratic equations relative to Z:

$$R = \frac{r_{12}^2 + r_{23}^2 Z_i^2 - 2 r_{12} r_{23} \cos\psi \cdot Z_i}{1 + r_{12}^2 r_{23}^2 Z_i^2 - 2 r_{12} r_{23} \cos\psi \cdot Z_i} \qquad (10)$$

$$T = \frac{T_{12} T_{23} Z_i}{1 + r_{12}^2 r_{23}^2 Z_i^2 - 2 r_{12} r_{23} \cos\psi \cdot Z_i} \qquad (11)$$

The solution of (11) gives:

$$Z_{1,2} = b/2a \pm \sqrt{\frac{b^2}{4a^2} - \frac{T}{a}} \quad , \qquad (12)$$

$$a = T r_{12}^2 r_{23}^2 \quad ,$$

$$b = T_{12} T_{23} + 2 T r_{12} r_{23} \cos\psi \quad .$$

Having replaced Z in equation (10) we find n as a root of a function

$$F = R - \frac{r_{12}^2 + r_{23}^2 Z_i^2 - 2 r_{12} r_{23} \cos\psi \cdot Z_i}{1 + r_{12}^2 r_{23}^2 Z_i^2 - 2 r_{12} r_{23} \cos\psi \cdot Z_i} \qquad (13)$$

Z value must meet $0 < Z < 1$ condition. In accordance to it, the sign in front of solution (12) root is chosen. After calculation n we find æ value according to the formula

$$æ_2 = \frac{-\lambda \cdot \ln Z_i}{4\pi d} \quad . \qquad (14)$$

The spectral dependencies, calculated both according to traditional and new formulae, are given in Figs 7-9. The former ones conform to data of [17], received by the same manner.

As it is shown in [18], R and T pair can yield up to four pairs of n and æ values, and a choice of correct val-

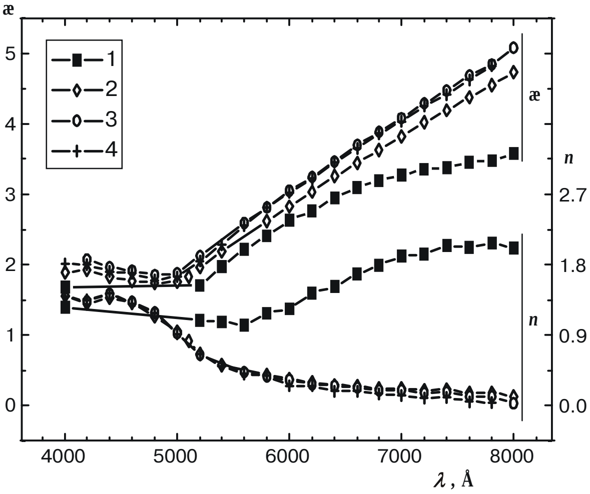

Fig. 7. Optical constants of gold films, calculated according to traditional formulae (root N1). The effective thicknesses of films are as follows: 1-85, 2-123, 3-132, 4-185Å.

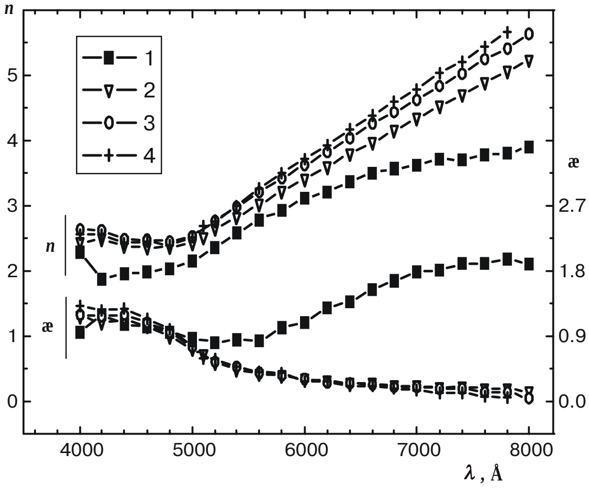

Fig. 8. Optical constants of gold films, calculated according to traditional formulae (root N2). Effective thicknesses of films are: 1-85, 2-123, 3-132, 4-185Å.

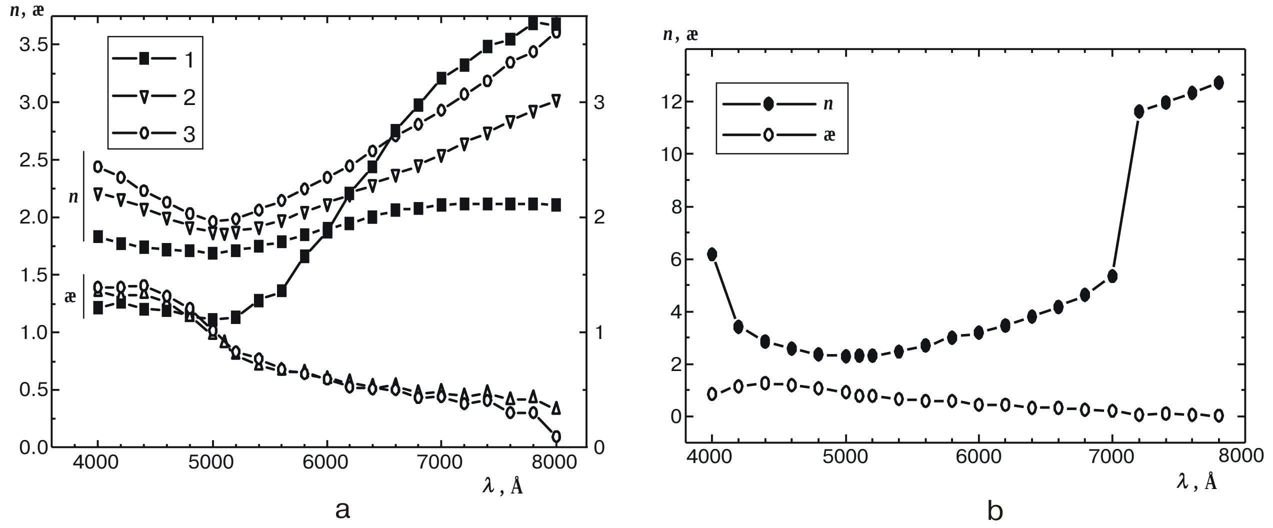

Fig. 9. Optical constants of gold films, calculated according to new formulae. Effective thicknesses of films are:
a) 1-85, 2-123, 3-132;
b) 185Å.

ues can be guided by physical conceptions. Two roots of $R(n,æ)$, $T(n, æ)$ equation systems are shown in Figs 7, 8.

According to the Drude theory, absorption coefficients of metals increase monotonously with the wavelength. However, in a visible region of a spectrum, absorption, caused by interband transitions, is superimposed on absorption by free careers. Moreover, in a case of thin samples, a certain role must be played by quantum-size effects. Apparently they take place for an 85Å thick film, which is commensurable with a half of de Broglie wavelength. Dependence of its corresponding curves n and æ differs significantly from that of the curves for other samples (Figs 7, 8). If we consider value $n < 1$ devoid any physical content, preference must be given to the second of the two roots. We consider it necessary to give values of both roots.

Calculations, which have been made due to a new theory (Fig. 9) give values of refraction coefficient $n > 1$ in the whole spectral interval of wavelengths investigated. A behavior of curve n for samples with $d = 185$Å (Fig. 9b). When $\lambda = 7000$ Å, it jumps up to higher values of n.

Conclusions

1. A study of the structure of gold films using the atomic-force microscope, shows that with the thicknesses used they are unbroken formations, and roughness (cavities and hills) does not exceed 30% from the layer thickness.

2. There were calculated optical constants n and æ for four films with different thicknesses in the spectral region $\lambda = 4000$-8000 Å. With this aim, experimental dependences of refraction and transmission coefficients were used; they were processed using two theories: the one worked on long ago, where energy factors of transmission and refraction at a boundary of two media are calculated using $\tilde{n} \rightarrow n \pm iæ$ substitution in Fresnel's formulae for transparent media; and a new theory, where these factors are calculated according to the formulae obtained from Maxwell's boundary conditions.

3. One of the traditional solutions leads to the values of refraction coefficient, which are less than unity, for three thicker samples (123, 132, 185Å), in a wide spectral region ($\lambda = 5000$-8000 Å). The curves $n = f(\lambda)$ for them are characteristic to coincide; it means that no dimensional effect is observed. A dispersion curve of the thinnest sample (85 Å) lies higher than $n = 1$ values, and in contrast to three above-mentioned curves, n-values increase with the rise of a wavelengths, getting at $\lambda \approx 7800$ Å over maximum, which shows the existence of size quantization.

Another solution by traditional method gives qualitatively contrasting results: for every wavelength the curves of refraction coefficient are situated higher than the absorption ones. In both cases the thinnest sample is marked with its behavior , and absolutely in the same way.

4. In accordance to the new theory, values of refraction coefficients in the whole spectral region exceed unity for every sample. A difference in the curve dependencies plotted using two theories, can be explained by absence of any dependence of refraction and transmission coefficients of separate boundaries in a new theory from absorption coefficient for normally incident rays.

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