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Dimensional effects in thin gold films

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Abstract. Research results of optical constants of thin gold films of different thickness are given in the paper. Their structure was studied using atomic-force microscope. Values of refraction n and absorption k coefficients were calculated from reflection and transmission spectra by traditional ratios, and using new theory as well. Comparison of results obtained by both methods was carried out and possible causes of divergences were pointed out.

Keywords: thin films, optical constants, size effects.

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1. Introduction

For many years calculation of optical constants of thin films has been based on relationships that consider multiple reflections 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. Although this method has been used for a long time, it is not free of deficiencies [1].

Transition from transparent to absorbing medium is postulated by introducing a complex refraction index $\tilde{n} = n \pm ik$. It may be this very substitution that leads to results which cause surprise. For example, with the reducing thickness of thin gold films [2-4] (Fig. 1) and atomic semiconductors [5-7], the refraction coefficient grows unlimitedly. Such a monotonous thickness dependence appears to be doubtful, while in a wide interval of thicknesses, used in the papers cited, at least one resonance maximum on $n = f(d)$ must take place. Calculations made according to traditional formulae [8] do not give such a maximum. For describing optical properties of granulated films, author of the paper [9] presents them as solid ones, with some effective mean-mass thickness, although this formula includes the geometrical one. Some doubts about application of Fresnel's formulae to island-like films were stated in paper [10], because those formulae, as authors believe, can lead to erroneous results because of fictitious nature of surfaces investigated.

While researching optical properties of bulk samples and thick films of many metals in wide regions of X-ray and optical spectra one obtains n values less than unity.

Data of papers [11-14] can be given as an example. 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 papers [13] and [14] monocrystals of gold and opaque aluminium films respectively are investigated.

Authors of the papers cited do not even try to prove reality of obtained values of optical constants. Examples given show necessity of searching for new approaches while solving optical problems of thin layers and solids in regions of intensive light absorption.

One of the new possibilities is discussed in paper [15]. Using integral equations that describe distribution of electromagnetic waves in conducting media, authors obtained a formula for a complex index of metal refraction. Unfortunately, spectral dependencies of refraction and absorption values, calculated by the authors, describe the experiment only at a qualitative level. Theory and experiment divergence could be a consequence of an assumption that a wave is flat, or, as authors say, involving quantum theory is necessary for more precise, quantitative agreement between the theory and experiment.

Below, we used data of the paper [16] for processing experimental results. Using Maxwell's boundary conditions, its author got analogs of Fresnel's formulae for absorbing media without applying $\tilde{n} \rightarrow n \pm ik$ substitution. By calculations according to these formulae obtained earlier [5-7] , of the experimental curves of transmission and reflection of Te, Se, Ge thin films, the thickness dependences of optical constants n and k [15] were determined. They differ principally from dependences 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.

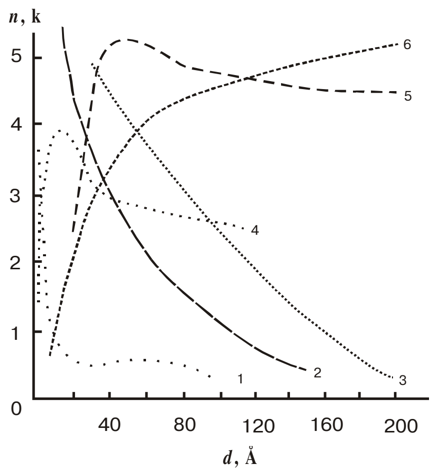

Fig. 1. Optical constant dependences on gold layer thicknesses for λ = 7000 Å: 1, 2 – n and k from [2]; 3, 4 – n and k [3]; 5, 6 – n and k [4], respectively.

At a first glance, the last example may seem to show suitability of new formulae [16] for determining optical constants of solids in spectral regions of intensive absorption. However, as it will be shown in further discussion of some results, they do not withdraw the existing difficulties and lack of critical analysis as well.

2. Structure of samples and method of measurements

Samples of different thickness were produced by thermal evaporation of gold in vacuum $\sim 1 \cdot 10^{-6}$ Torr on quartz and glass substrates at room temperature. The purity of initial material was not worse than 99.99%. The deposition rate was 1-10Å/c. In the process of deposition the thickness of films was controlled using a quartz resonator, and right after deposition was measured by an atomic-force microscope.

In Fig. 2 the structure and distribution of irregularities of the thinnest gold films (20Å) , obtained using the same microscope, are represented. As it can be seen, cavities met along the drawn line, make up less than 30% from the film's thickness. For a better visible relief perception, a sample region 500×500 nm^2 in axonometric projection is represented in Fig. 3 with somewhat stretched scale along the vertical line. A light roughness observed is also characteristic for other samples.

Structure of the thicker sample d = 85Å is represented in Fig. 4. Here juts, characteristic of thick gold films, are already clearly seen.

Scanning over a larger area (5×5µm^2) showed no islands, so we can consider that every film has a plain surface, while dimensions of unevennesses are significantly smaller than λ. From the substrate's side mirroring of the layers is better. Therefore while processing experimental data, Fresnel's formulae can be easily used.

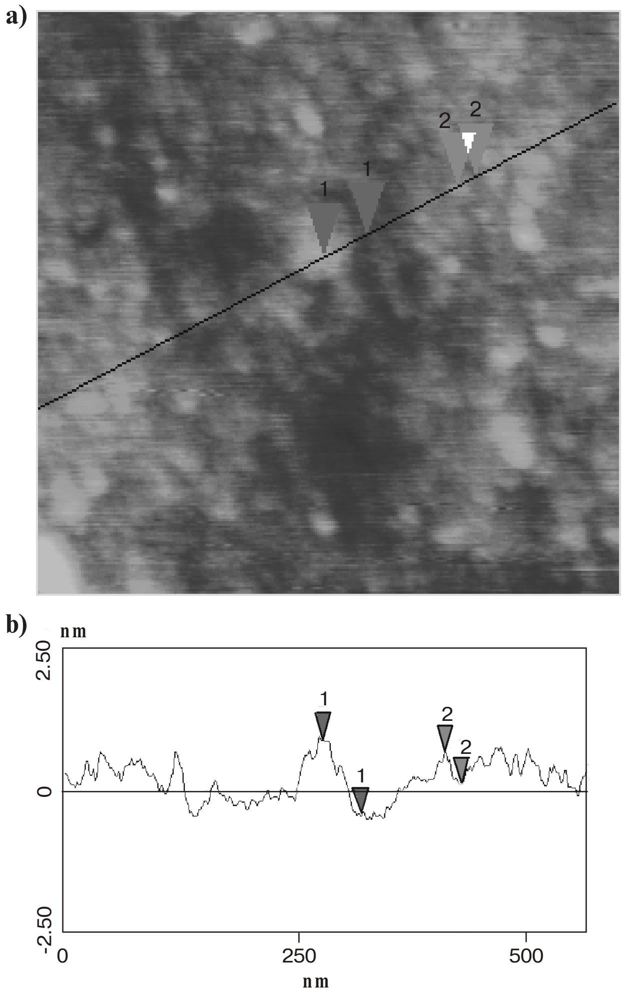

Fig. 2. a) Look of gold film surface with a scanned direction (area of 500×500 nm^2, thickness of the film 20 Å);
b) Distribution of irregularities along the indicated direction.

Angular dependences of energy coefficients R_p and R_s, a light wave, polarized in a plane of incidence and a surface, perpendicular to it, were measured on a device with a goniometer GS-5. Helium-neon laser LG-79 was used as a source of emission, and application of precision «current-voltage» transformer let increase accuracy of measurements to 0.1%.

Spectral dependences of reflection R and transmission T coefficients of the light wave for layer-substrate system were measured using a set based on a monochromator MDR-23 in a 4000-8000 Å interval with 1% error.

Optical constants of thin gold layers n and k were calculated using traditional [8] and new relationships [16], namely:

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

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

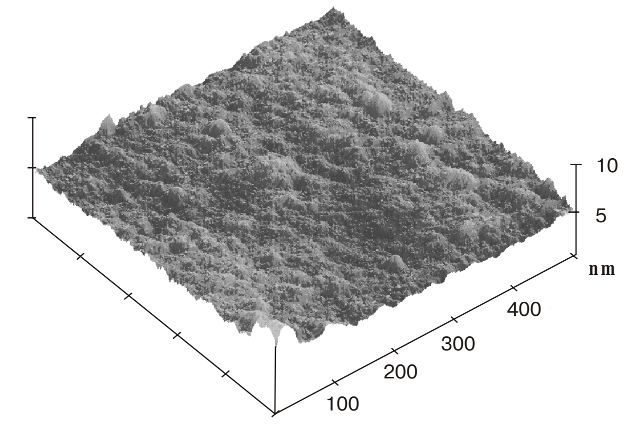

Fig. 3. The same film surface as in Fig. 2 but in axonometric projection.

$$a = T r_{12}^2 r_{23}^2 \quad (3)$$

$$b = T_{12} T_{23} + 2 T r_{12} r_{23} \cos\psi \quad (4)$$

$$\psi = \frac{4\pi}{\lambda} n_2 d \quad (5)$$

$$r_{12} = \frac{n_2 - n_1}{n_2 + n_1}; \; r_{23} = \frac{n_3 - n_2}{n_3 + n_2} \quad (6)$$

$$t_{12} = \frac{2n_1}{n_2 + n_1}; \; t_{23} = \frac{2n_2}{n_3 + n_2} \quad (7)$$

Here index 1 corresponds to air, 2 - to the film, 3 - to the substrate, *R*, *T* are the experimental values of reflection and transmission.

According to theory demands, Z_i value must satisfy $0 < Z_i < 1$ condition, fulfillment of which is determined by the sign before the root (2). After having solved equation (1) by numerical method and having defined n_2 , k_2 value is found by the formula

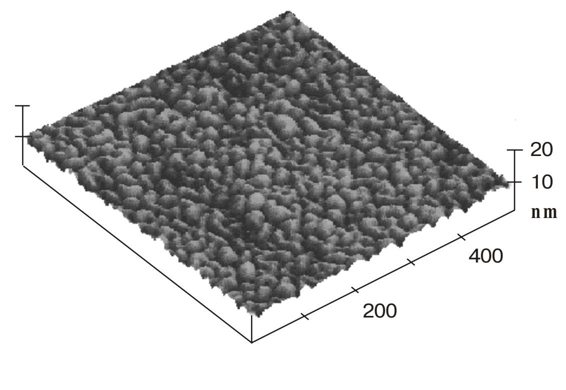

Fig. 4. Structure of a thicker film (d = 85Å) obtained with AFM.

$$k_2 = \frac{-\lambda \cdot \ln Z_i}{4\pi d} \quad (8)$$

Following to the expressions (6) and (7), in contrast to the old theory, the amplitude factors of reflection and transmission of certain boundaries in the new theory [16] 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, n, and absorption, coefficients k, of the layer. (Below we will omit index 2 at n and k). The fact of a normal incidence having some anomalous properties arouses surprise.

At such approach, as the author of the new theory states, having measured the reflection energetic coefficient at a normal light incidence on a bulk sample, refraction coefficient can be easily calculated by the formula:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (9)$$

Thickness dependences $n = f(d)$ and $k = f(d)$ were calculated by matrix method [19], based on traditional formulae. Its advantage lies in using 40-80 pairs of experimental values R_s and R_p for angles from 6 to 87°, providing a solution stability and high accuracy of finding n and k values. Such average optical constants were used for determining R and T values, necessary for calculation of thickness dependence of optical constants by the new theory formulae.

3. Results and their discussion.

As it is shown in [20], R and T pair measured values can yield up to four pairs of n and k values, and a choice of correct values can be guided by physical conceptions. For example, in our case from two roots of $R(n,k)$, $T(n,k)$ equation system we chose the one, for which $n<k$, because the chosen interval of waves length is situated at much longer wavelengths than λ_p, that is the wavelength of plasma resonance, falling in to the UV spectrum region for gold.

Absorption spectra (A=1–R–T) of gold films, deposited on quartz substrates, are shown in Fig. 5. Their thicknesses are given in the insertion. With thickness increasing, absorption ability, as it was expected, grows. Besides, the maximum observed moves to a region of longer waves. The curve, that characterizes absorption of the thickest film, makes up the exception. Its maximum absorption corresponds to the most shortwave region of a visible spectrum., and can be compared to the film absorption, thickness of which is only 3Å, that is five times smaller.

The described character of absorptivity A change with d and λ changing is connected with three factors: structure, absorption by free carriers and quantum transitions between allowed energy bands. In its turn, the latter two

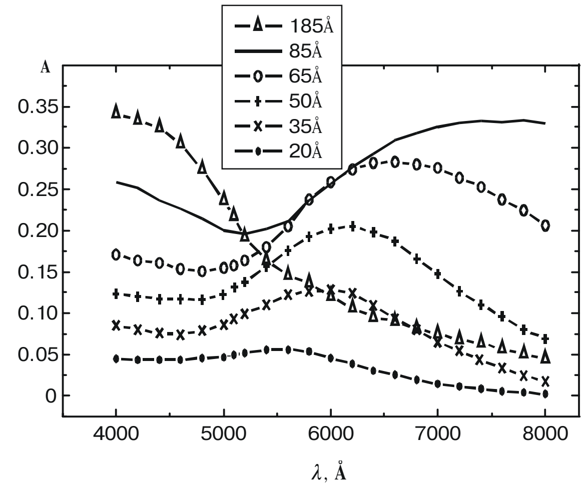

Fig. 5. Absorption spectra of gold films deposited on silica substrates.

mechanisms undergo the influence of a thickness factor. With the latter one decreasing the length of carriers free path decreases, what influences their contribution to general absorption. Besides, with the thickness changing, renormalization of wave function takes place, which characterize bands of allowed energies. Electron's quasi-momentum component perpendicular to the film plane is quantized, obtaining only specific values. The same happens with energy. As a result, dependence of energy, absorbed by the film in wavelength scale for different thicknesses will be different, which is shown in Fig. 5.

A set of gold films transmission curves of eight different thicknesses is given in the next figure. Apart from the represented in Fig. 5 , thicknesses 123Å and 135 Å are represented here in addition, for which absorption curves are close to the film curve 185 Å thick, therefore they were not given in Fig. 5.

We must not be surprised at the fact that absorption curves for three thickest films appeared to be closely situated. The matter is that with the thickness changing, redistribution of intensities between a reflected and passed through the layer waves takes place. Therefore, transmission curves can appear to be more displaced relatively to one another than absorption curves. On transmission curves both maxima and minima are observed, and the latter ones are characteristic for thinner films. This very transmission behavior, depending on the thickness, is characteristic when dimensional quantization of energy states is available.

According to measured transmission and reflection curves, spectral and thickness dependences of optical parameters n and k were calculated. Results, obtained using traditional formulae, are given in Fig. 7 for films of four thicknesses. Each one has at least one extremum. Values of refraction indexes are grouped around n=1 value. In some regions of wavelengths they reach 2 (a film 85 Å thick), or close to zero (films 20 Å and 185 Å thick). The highest values are characteristic for the thickest film, which correlates with its smallest n values. At this very n and k relationship the film has a high reflection ability in the corresponding spectral region (λ = 6000÷8000 Å).

Spectral dependences of researched films optical parameters, calculated by formulae of the new theory, are given in Fig. 8. This theory has in advance a condition, that excepts n <1 value. All curves for n are situated higher than n = 1.5 value. With the thickness increasing a general tendency to an increase of the refraction factor takes place. As to k, its behavior is somewhat more complicated. At λ = 5000 Å all dependences have in fact one common point with k =1 value. Behind it, k of the thinnest samples passes through the maximum, in a long-wave region. However, for a film 85 Å thick it is only outlined on the very edge of the spectral interval used. In the whole region two thickest films show monotonous decrease of k

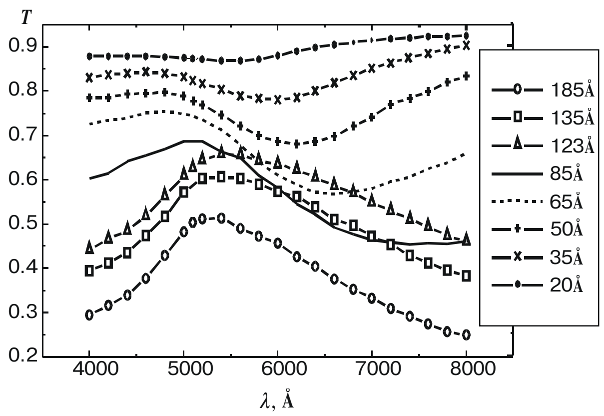

Fig. 6. Spectral dependences of gold film transmission.

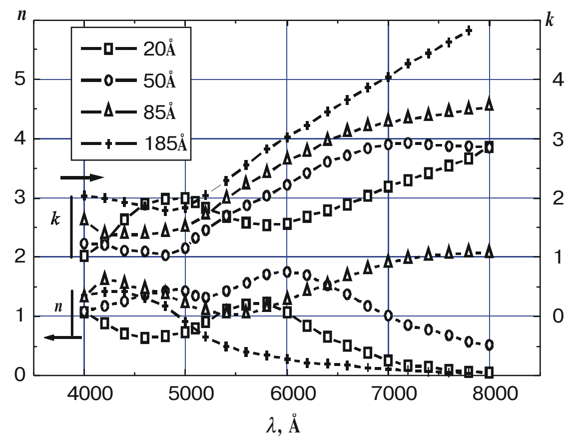

Fig. 7. Spectral dependences of film optical constants calculated using traditional formulae [8].

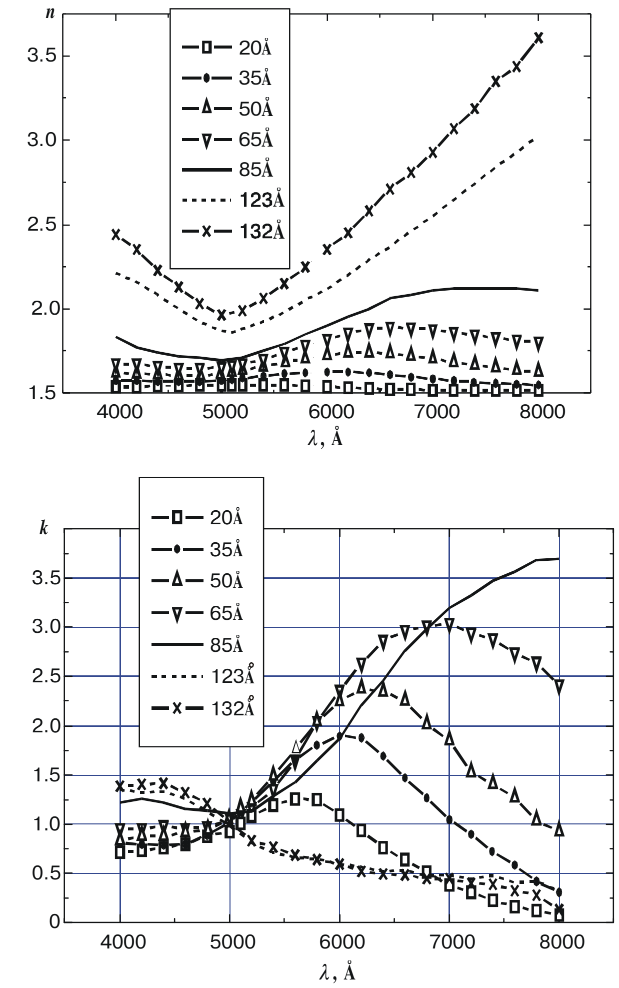

Fig. 8. Spectral dependences of gold film optical constants calculated using formulae [16].

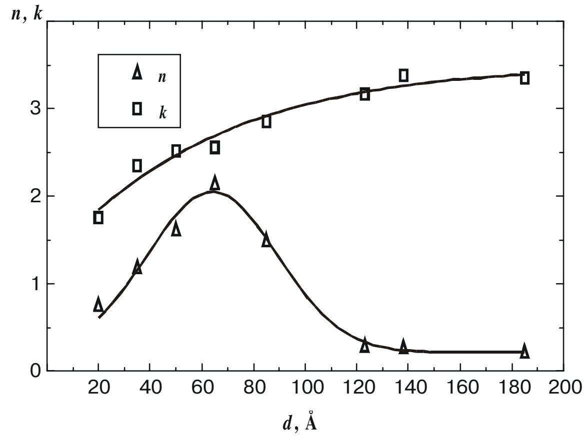

Fig. 9. Thickness dependences of gold film optical costants calculated using traditional formulae [8] for λ = 6328Å

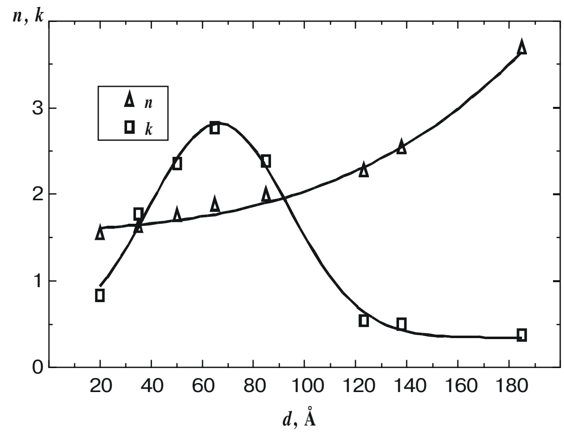

Fig. 10. Thickness dependences of gold film refraction and absorption indexes calculated using new formulae [16] for λ = 6328Å.

with λ increasing.

Taking into account results obtained by using both theories we come to a conclusion that generally non-monotonous dependencies n and k with a change of the wavelength are caused by presence of dimensional quantization effect with a certain superposition of quantum transitions between allowed bands.

Interference contribution is not significant even for the thickest sample at refraction coefficient 2, because by estimations a path difference appears to be insignificant for creating an interference maximum of the first order. This conclusion is more adequate while analysing results, received using traditional formulae for calculation n and k, while they lead to lower values of refraction coefficients.

Thickness dependencies n and k for a number of wavelengths were studied in the paper. They all have qualitatively similar character, therefore we give dependences only for λ = 6328 Å. As it follows from Fig. 9, based on traditional formulae, refraction factor passes through the maximum, corresponding to $d \approx 70$Å thickness. It falls monotonously from the left and from the right sides, and beginning with 125 Å thickness it remains without changes. In the same thickness interval k, within measurement errors as well, remains constant and slowly falls with the layer thickness decreasing.

A diametrically contrasting view was received by the new theory (Fig. 10). As in the previous case, a symmetric maximum is characteristic not only for the refraction index, but for the absorption one, too. On the contrary, refraction index grows monotonously with the thickness, passing values approximately from 1.5 to 4.

Conclusions

The main question, which arises from the discussion just held, is as following: which theory should be preferentially given to while calculating optical constants of thin films? Calculation using traditional formulae leads to a hardly apprehensible abrupt increase of refraction index with the layer thickness decreasing. This very dependence was deduced by three different authors for thin gold films [2-4], as well as in papers [5-7] for atomic semiconductors. Because with d decreasing to zero, films acquire a two-dimensional hel structure, substance density in which is much lower than the one of a bulk sample, a qualitatively contrary thickness dependence of n should be expected. Such a kind of the considered dependence was obtained for atomic semiconductors at calculations based on the same experimental curves R and T, as well as using the new theory. Besides, the author of the new theory showed its applicability for solving problems of another type without using additional boundary conditions while describing supplementary light waves in CdS monocrystal [21].

But serious objections are caused by introducing formulae (6), (7) and (9) for a boundary, which separates transparent and absorbing media, at a normal light beam incidence on it.

Summing up, we consider necessary further attempts in development of optical phenomena theory for thin absorbing films and bulk samples in regions of intensive light absorption.

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References

1. J.I. Larruquert, J.A. Mendez and J.A. Aznarez, Far-ultraviolet reflectance mesurements and optical constants of unoxidized aluminum films // *Appl. Opt.* **34**(22), pp. 4892-4899 (1995).
2. W.D. Werener, B.M. Leadon, *Rev. Scient. Instr.,* **24**(2), p.121 (1953); E.H. Winkel. *Rev. Scient. Instr.* 24(11), p.1067 (1953).
3. I. Krautkrämer. *Proc. Phys. Soc.* **32**, p. 537 (1938).
4. B. Pogany . *Ann. d. Phys.* **49**, p. 537 (1916).
5. M.P. Lisitsa, N.G. Tsvelykh, Optics of thin film (II Te) // *Optika i spektroskopiya* **4**(3), pp.373-377 (1958), (in Russian).
6. M.P. Lisitsa, V.M. Mayevsky, N.G. Tsvelykh, Optics of thin film (III Se) // *Optika i spektroskopiya* **5**(2), pp.179-183 (1958), (in Russian).
7. M.P. Lisitsa, N.G. Tsvelykh, Optics of thin film (IV Ge) // *Optika i spektroskopiya* 5(5), p.622 (1958), (in Russian).
8. H. Murman. *Zeitschr. f. Phys*. **80**, p. 167 (1933).
9. E. Kretschmann // *Ztschr. Phys*., **221**, pp. 346-356 (1969).
10. T. Yamaguchi, H. Takahashi, A. Sudoh // *J. Opt. Soc. Amer*., **68**, pp. 1039–1044 (1978).
11. P.B. Johnson, R.W. Christy, Optical constants of noble metals // *Phys. Rev. B* **6**(12), pp. 4370-4379 (1972).
12. I.N. Shklarevsky, R.G. Yarovaya, Quantum light absorption in gold // *Optika i spektroskopiya* **21**(2), pp. 197-203 (1966), (in Russian).
13. M.Otter. *Zs. Phys.* **161**, pp. 163 (1961).
14. A.D. Rakic, Algorithm for the determination of intrinsic optical constant of metal films: application to aluminum // *Appl. Opt*. **34**(22), pp. 4755-4767 (1995) (in Russian).
15. O.N. Gadomsky, U. U. Voronov, Reflection and refraction of light on the surface of metal // *Optika i spektroskopiya* **87**(6), pp. 1017-1023, (1999) (in Russian).
16. T.A. Kudykina, Bondary conditions in case of electromagnetic wave absorption // *Phys. Stat. Sol* (b) **160**, pp. 365-373 (1990); Optical properties of semiconductors (Ge, Se, GaAs, InSb) **165**, pp. 591-598 (1991).
17. T.A. Кudyкina, M.P. Lisitsa, Dimension dependence of thin films Ge, Si, Se, Te // *Optoelectronika i poluprovodnikovaya tekhnika*, pp. 106-114, (1997) (in Russian).
18. U.I. Petrov. Absorption of light by small particles // *Optika i spektroskopiya* **27**(4), p. 665 (1969), (in Russian).
19. R. Azzam, N. Bashara, *Elipsometry and polarized light.* Mir, Moscow, 1981 (in Russian).
20. M.H. Francomb, R .W. Hofman, Optical characteristics of metal films. In: *Fizika tonkikh plenok*, **Vol. VI**, F. Abeles, p. 210, Mockow, Mir, 1973 (in Russian).
21. V.L. Vinnetsky, T.A. Kudykina, Three light waves in region of exciton resonances in CdS crystals // *Fizika i tekhnika poluprovodnikov* **23**(10), p. 1910 (1989) (in Russian).