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OPTICS OF LOW-DIMENSIONAL STRUCTURES, MESOSTRUCTURES, AND METAMATERIALS

Optical Coefficients of Nanoscale Copper Films in the Range of 9–11 GHz

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Abstract—The reflectance, transmittance, and absorption coefficient of ultrathin copper films on a quartz substrate have been measured in a waveguide at frequencies of 9–11 GHz. Films less than 5 nm thick are oxidized almost completely and transparent to microwave radiation. A conducting layer is formed at a film thickness above 5 nm; however, the reflectance increases with thickness in the range of 5–15 nm more slowly than is yielded by calculations using the model conductivity of a continuous film. These results can be explained by the film morphology.

Keywords: complex permittivity, effective medium, microwave range

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INTRODUCTION

The interaction of electromagnetic radiation with nanoscale metal films is accompanied by the size effect, which manifests itself in anomalously high (up to 50%) absorption of the incident radiation [1]. The film thickness corresponding to the absorption maximum is several nanometers, which is much smaller than the skin depth. A detailed review of the optical properties of ultrathin metal films in microwave and THz ranges, as well as the current state of theoretical description of the size effect in films and experimental results, were presented in [2]. The uniqueness of ultrathin films is represented by the independence of their absorbing properties from frequency in a wide wavelength range and weak dependence on the metal type [1–3]. Examples of application of the effect of strong absorption of electromagnetic waves by ultrathin metal films in various devices were also given in the review. One of these applications is a thermoacoustic detector of nano- and microsecond pulses, where aluminum [4] and chromium [5] nanofilms are used as the sensing element. These detectors operate at room temperature and have almost identical sensitivities in the centimeter and millimeter ranges.

Copper, which is characterized by high conductivity, is widely used for producing microelectronic devices. Microminiaturization of basic elements of integrated circuits and increase in their surface density require reduction of the length and thickness of conducting elements. The use of copper conductors and contacts with a thickness of several nanometers is significantly constrained by their oxidation in air [6]. Investigation of the kinetics of conducting properties of copper films depending on their thickness, deposition method, and substrate structure is of great interest for technological processes using nanofilms [7]. Measurements of the optical coefficients of ultrathin films in a waveguide in the centimeter [8, 9] and millimeter [1] ranges make it possible to trace the kinetics of formation of an oxide layer, estimate its thickness, and determine the conductivity of the film depending on its thickness. The accuracy and reliability of such studies are currently increased by means of vector network analyzers, which allow one to measure the complex reflectance and transmittance in a wide frequency range. The purpose of this study was to investigate the conductivity of copper films prepared by magnetron sputtering in the thicknesses range from 1 to 30 nm. To this end, we measured the reflectance, transmission, and absorption coefficient of films on quartz substrates placed in a waveguide with a bandwidth of 8–12 GHz. The measurement results were compared with the values calculated using different model dependences of the film conductivity on the thickness.

CALCULATION OF THE REFLECTANCE AND TRANSMITTANCE OF A METAL FILM ON A DIELECTRIC SUBSTRATE IN A WAVEGUIDE

We consider a structure composed of metal film *2* on dielectric substrate *3* with thicknesses h_2 and h_3,

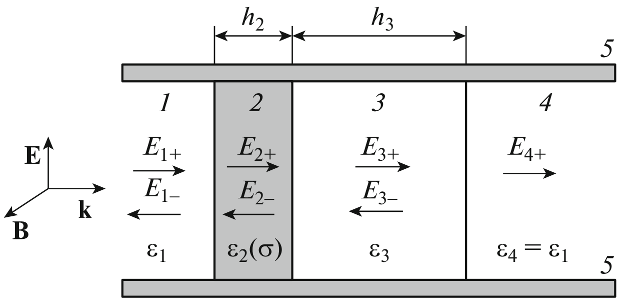

Fig. 1. Model used in the calculations: (*1*, *4*) air, (*2*) copper film with thickness h_2, (*3*) quartz substrate with thickness h_3, and (*5*) rectangular waveguide.

respectively (Fig. 1). The structure is in a rectangular waveguide, where an electromagnetic TE_{10} wave propagates. The wave with wave vector **k** is incident from medium *1*, passes through layers *2* and *3*, and emerges into medium *4*. Waves reflected from the corresponding boundaries arise in media *1–3*. Each medium is characterized by conductivity σ, relative permittivity ε, and relative permeability μ. We will consider nonmagnetic media, where the relative permeability is $\mu = 1$. In each medium, the Helmholtz equations are valid for complex amplitudes of the electromagnetic field vectors; solutions to these equations are superposition of the waves propagating in opposite directions: $\hat{E}_x(z) = \hat{E}_+ e^{ikz} + \hat{E}_- e^{-ikz}$. Here, $k = k' + ik''$ is the complex wavenumber of the electromagnetic wave. Using the conditions of continuity of the tangential vector components of the electric and magnetic field strengths at interfaces of the media, one can derive the following system of equations for the complex amplitudes in each medium:

$$\hat{E}_{1+} + \hat{E}_{1-} = \hat{E}_{2+} + \hat{E}_{2-},$$

$$k_1(\hat{E}_{1+} - \hat{E}_{1-}) = k_2(\hat{E}_{2+} - \hat{E}_{2-}),$$

$$\hat{E}_{2+} e^{ik_2h_2} + \hat{E}_{2-} e^{-ik_2h_2} = \hat{E}_{3+} e^{ik_3h_2} + \hat{E}_{3-} e^{-ik_3h_2},$$

$$k_2(\hat{E}_{2+} e^{ik_2h_2} - \hat{E}_{2-} e^{-ik_2h_2}) = k_3(\hat{E}_{3+} e^{ik_3h_2} - \hat{E}_{3-} e^{-ik_3h_2}),$$

$$\hat{E}_{3+} e^{ik_3(h_2+h_3)} + \hat{E}_{3-} e^{-ik_3(h_2+h_3)} = \hat{E}_{4+} e^{ik_4(h_2+h_3)},$$

$$k_3(\hat{E}_{3+} e^{ik_3(h_2+h_3)} - \hat{E}_{3-} e^{-ik_3(h_2+h_3)}) = k_4(\hat{E}_{4+} e^{ik_4(h_2+h_3)}).$$

Complex amplitude reflectance r and transmittance t are determined by solving this system of equations:

$$r = \hat{E}_{1-}/\hat{E}_{1+} = \frac{DG_- + FG_+}{DG_+ + FG_-} = |r| e^{i\varphi_r},$$

$$t = e^{ik_4(h_2+h_3)} \hat{E}_{4+}/\hat{E}_{1+} = \frac{2e^{ik_4(h_2+h_3)}}{DG_+ + FG_-} = |t| e^{i\varphi_t},$$

where the following coefficients are introduced:

$$G_\pm = \left[1 \pm \frac{k_2}{k_1}\right],$$

$$D = A_+C_+ + A_-C_-, \quad F = B_+C_+ + B_-C_-,$$

$$A_\pm = \frac{1}{2} e^{\pm i(k_3 \mp k_2)h_2} \left[1 \pm \frac{k_3}{k_2}\right],$$

$$B_\pm = \frac{1}{2} e^{\pm i(k_3 \pm k_2)h_2} \left[1 \mp \frac{k_3}{k_2}\right],$$

$$C_\pm = \frac{1}{2} e^{i(k_4 \mp k_3)(h_2+h_3)} \left[1 \pm \frac{k_4}{k_3}\right].$$

The energy reflectance, transmittance, and absorption coefficient were calculated from the formulas $R = |r|^2$, $T = |t|^2$, $A = 1 - R - T$.

The reflectance and transmittance were measured in a 3-cm rectangular waveguide 10 × 23 mm in size. In the frequency range of 8–12 GHz, the TE_{10} wave propagates in the waveguide with the wavenumber that can be written in the form $k_i = \sqrt{k_{0i}^2 - (\pi/a)^2}$, where k_{0i} is the wavenumber of the wave in free space, a = 23 mm is the size of the long waveguide side, and subscript i indicates the medium of wave propagation. The wavenumbers of the TE_{10} wave in air (i = 1 and 4), metal film (i = 2), and quartz substrate (i = 3) can be written as

$$k_1 = k_4 = \sqrt{(\omega/c_0)^2 - (\pi/a)^2},$$

$$k_2 = \sqrt{\omega^2\varepsilon_2/c_0^2 - (\pi/a)^2}, \quad k_3 = \sqrt{\omega^2\varepsilon_3/c_0^2 - (\pi/a)^2},$$

where c_0 is the speed of light in vacuum and ε_0 = 8.85 pF/m is the permittivity of free space. It was assumed that the relative permittivity is $\varepsilon_1 = \varepsilon_4 = 1$ for air and $\varepsilon_3 = 3.8$ for the quartz substrate in the range of 8–12 GHz [10]. The complex copper-film permittivity for microwave frequencies was calculated from the formula

$$\frac{\varepsilon_2(\omega)}{\varepsilon_0} = (1 - [(\varepsilon_0\omega_p/\sigma)^2 + (\omega/\omega_p)^2]^{-1})$$
$$+ i\varepsilon_0\omega_p^2/\sigma\omega[(\varepsilon_0\omega_p/\sigma)^2 + (\omega/\omega_p)^2],$$

where ω_p is the plasma frequency of free electrons in the metal, $\omega_p^2 = n_e e^2/m\varepsilon_0$; n_e is the free-electron concentration; m is the electron mass; e is the elementary charge; and σ is the copper-film conductivity, which is a function of the thickness. In copper, $n_e = 8.47 \times 10^{28}$ m^{-3} and $\omega_p = 1.6 \times 10^{16}$ rad/s. The dependence of

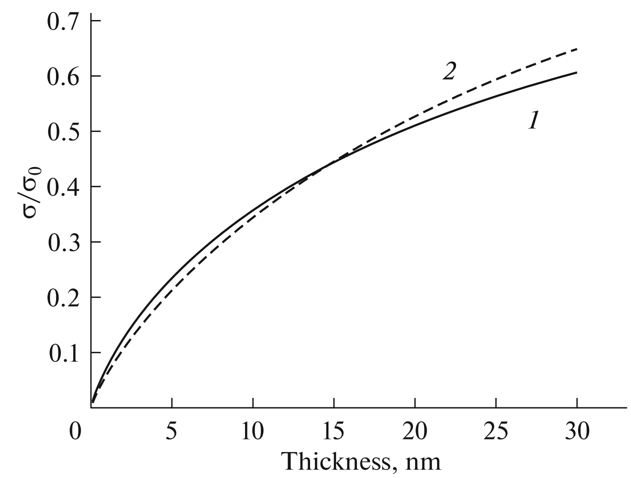

Fig. 2. Model dependence of the conductivity of the copper film on its thickness calculated from the exact (curve *1*) and approximate (curve *2*) formulas.

the film conductivity on thickness $\sigma(h)$ was calculated from the formula proposed in [11, 12]:

$$\frac{\sigma(h)}{\sigma_0} = 1 - \frac{3}{2\alpha}\int_1^\infty (\eta^{-3} - \eta^{-5})(1 - e^{-\alpha\eta})d\eta$$
$$= 1 - \frac{3}{8\alpha} + \frac{e^{-\alpha}}{16\alpha}(6 - 10\alpha - \alpha^2 + \alpha^3) \quad (1)$$
$$+ \frac{\alpha}{16}(12 - \alpha^2)Ei(\alpha),$$

where $\sigma_0 = 5.9 \times 10^7$ Sm/m is the bulk-metal conductivity, $\alpha = h/l_0$ is the ratio of the film thickness to the electron mean free path in the metal bulk ($l_0 = 42$ nm in copper), and $Ei(\alpha) = \int_\alpha^\infty \exp(-\eta)/\eta d\eta$ is the exponential integral. This dependence is shown by the solid curve in Fig. 2. Approximate formula (2), where the dependence of the conductivity on parameter α is clearer, is often used instead of (1):

$$\frac{\sigma(h)}{\sigma_0} = 0.5\alpha(1.5 + \ln(1/\alpha)), \quad \alpha \le 1,$$
$$\frac{\sigma(h)}{\sigma_0} = 1 - 0.25\alpha, \quad \alpha > 1. \quad (2)$$

EXPERIMENTAL SETUP AND MEASUREMENT METHODS

The copper films were deposited in a Leybold Z-550 vacuum system with the preliminary residual pressure of 10^{-5} mbar by magnetron sputtering. A target with a degree of purity of 99.999% and 2-mm-thick quartz substrates 22.9 × 9.8 mm in size were used. Before being placed into the chamber, the substrates were treated in 10% solution of hydrogen peroxide, washed with distilled water, and dried under nitrogen flow. During the deposition, the argon pressure in the chamber was maintained equal to 4 μbar. The substrates were fixed in a cooled holder at a distance of 6 cm from the target and rotated with a frequency of 4 rpm to obtain films with a thickness uniformly distributed over the entire surface. The copper film thickness was calculated from the target sputtering rate, which was 2 nm/min at a dc power of 100 W. Films with the following thicknesses were prepared: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0, 7.5, 10, 20, and 30 nm.

The optical coefficients of the copper films on substrates were measured in a rectangular waveguide in the frequency range of 9–11 GHz (Fig. 3a). The substrates with films *1* were mounted at the end of measuring waveguide *2* so that the films are oriented along the incident-wave direction. The substrate sizes were chosen to be 22.9 × 9.8 mm so as to completely overlap the waveguide cross section. To calibrate the channel at total reflection, the substrate was replaced with a copper plate with the sizes equal to those of the quartz substrate. The waveguide was connected to ports of the ZVA-24 vector network analyzer via two coaxial waveguide adapters *3* and *4*. The amplitude and phase of the scattering parameters S_{11} and S_{12} were measured at discrete frequencies in the range of 9–11 GHz with a step of 0.5 GHz for the substrates with the films with different thicknesses placed in the measuring waveguide. For the channel calibration, the scattering parameters were measured at each frequency in the measuring waveguide containing a pure substrate without film and a copper plate completely reflecting the radiation. Reflectance *R*, transmittance *T*, and absorption coefficient *A* were calculated from the formulas

$$R = \left(\frac{S_{11\mathrm{F}}}{S_{11\mathrm{M}}}\right)^2, \quad T = \left(\frac{S_{12\mathrm{F}}}{S_{120}}\right)^2, \quad A = 1 - R - T,$$

where $S_{11\mathrm{F}}$ and $S_{11\mathrm{M}}$ are the amplitudes of parameter S_{11} measured in the measuring waveguide containing the substrate with the film and metal plate, respectively, and $S_{12\mathrm{F}}$ and S_{120} are the amplitudes of parameter S_{12} measured in the waveguide with the metal film on the substrate and without it, respectively.

RESULTS

Figure 4 shows the dependences of the optical coefficients of the copper films on quartz substrate on the film thickness calculated for copper bulk conductivity $\sigma_0 = 5.9 \times 10^7$ Sm/m. Zero thickness ($h = 0$) corresponds to the pure substrate without film. The dependences obtained at a frequency of 10 GHz for the film thickness up to 30 nm are presented in Fig. 4a. At a film thickness exceeding 10 nm, the copper reflectance and transmittance approach the values that are typical of solid metal, and the absorption coefficient does not exceed 0.05. The absorption coefficient rapidly increases with an increase in the film thickness to

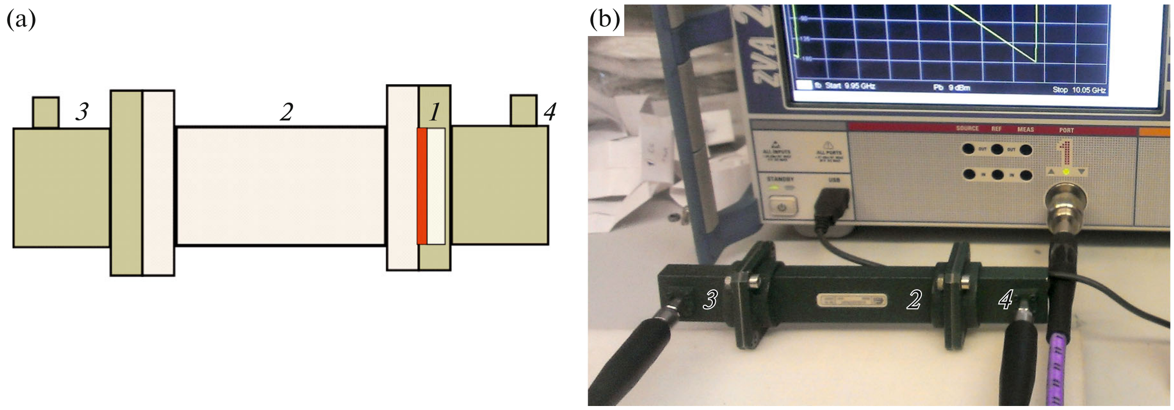

Fig. 3. (a) Schematic and (b) photograph of the experimental setup for measuring the reflectance and transmittance of the copper films: (*1*) substrate with the copper film, (*2*) waveguide, and (*3*, *4*) coaxial waveguide adapters.

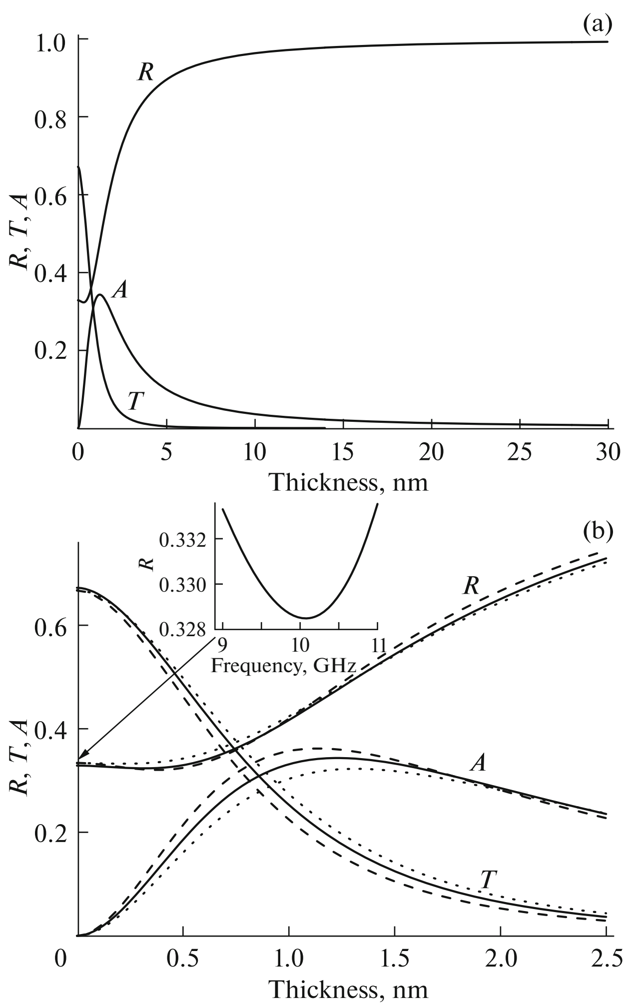

Fig. 4. Calculated dependences of the optical coefficients on the copper film thickness (a) at a wave frequency of 10 GHz in the thickness range of 0–30 nm and (b) at frequencies of (dashed line) 9, (solid line) 10, and (dotted line) 11 GHz for film thicknesses from 0 to 2.5 nm. The dependence of the quartz-substrate reflectance on frequency in the range of 9–11 GHz is shown in the inset.

1.24 nm to reach the maximum value of 0.34. The more detailed behavior of the optical coefficients is shown in Fig. 4b. A specific feature of measurements of the optical coefficients of films on a dielectric substrate in a waveguide is the presence of the waveguide dispersion of the electromagnetic-wave velocity. This manifests itself in the frequency dependences of the reflectance and transmittance of the pure substrate. The reflectance has a minimum near the frequency of 10 GHz (shown in the inset in Fig. 4b). The values at frequencies of 9 and 11 GHz exceed this minimum by 1.6%, which can be measured. Note that the quartz substrate in the waveguide reflects almost 33% of the incident energy, which exceeds reflection from the substrate in free space; this fact must be taken into account when carrying out waveguide measurements. The minimum reflectance corresponds to the film thickness of 0.32 nm. Its value is smaller by 0.5% than for the reflection from the substrate without film, i.e., a local bleaching of the film–substrate structure is observed. The waveguide dispersion yields the frequency dependence of absorption coefficient *A* of the film on the substrate. The maximum value of coefficient *A* increases by almost 11% with a decrease in the frequency from 11 to 9 GHz (Fig. 4b). All the above specific features should be taken into account when carrying out the measurements.

Figure 5 shows the measured dependences of the reflectance and transmittance of the copper films on substrate on the film thickness. Different symbols correspond to measurements in the waveguide at frequencies of 9, 10, and 11 GHz. Films with a thickness not exceeding 5 nm barely affect the wave reflection, which is determined only by the quartz-substrate parameters. The increase in the film thickness from 5 to 15 nm is accompanied by a rather fast increase in the reflectance and a decrease in the transmittance, which corresponds to the film transition from dielectric state to conducting. At the film thickness of

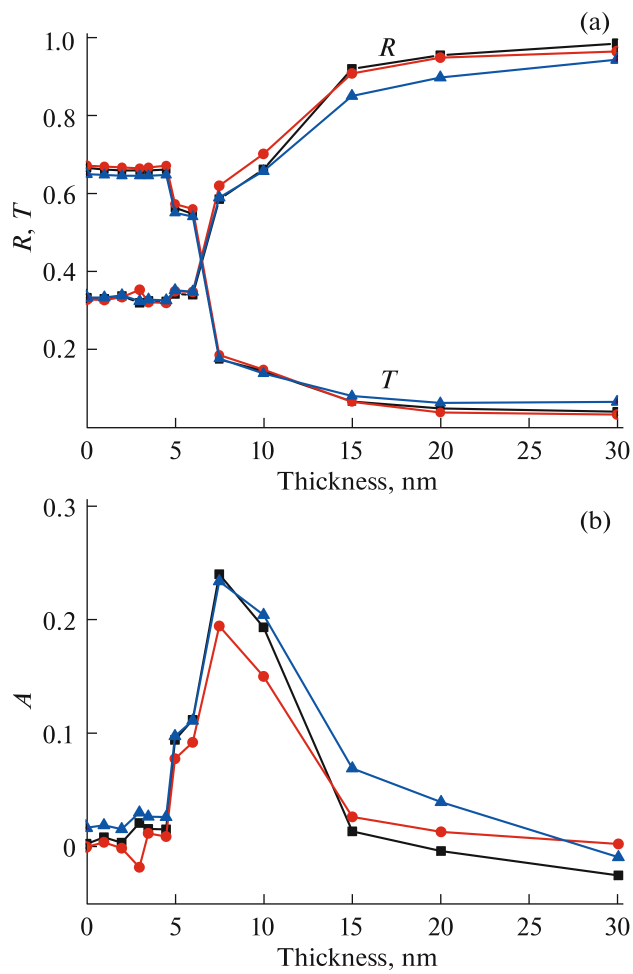

Fig. 5. Dependences of the (a) reflectance and transmittance and (b) absorption coefficient on the copper-film thickness measured at frequencies of (■) 9, (●) 10, and (▲) 11 GHz.

7.5 nm, one can observe a maximum absorption coefficient equal to about 25% of the incident wave energy.

The optical coefficients measured at a frequency of 10 GHz and the calculation results are compared in Fig. 6. According to the measurement results, the film transition from insulator to conductor begins at the film thickness of 5 nm. A continuous conducting surface, which can reflect electromagnetic radiation, is formed on the films, the thickness of which exceeds 5 nm. For the comparison with the measured values, the calculated curves are shifted by a thickness of 5 nm. Note that the measured reflectance and transmittance of the pure substrate coincide with the calculated values at all frequencies with an error not exceeding 2%. This result was provided by accurate calibration of the measuring channel and substrate orientation completely perpendicular to the incident radiation. At the film thickness of 30 nm, the measured reflectance (0.96) and transmittance (0.03) cor-

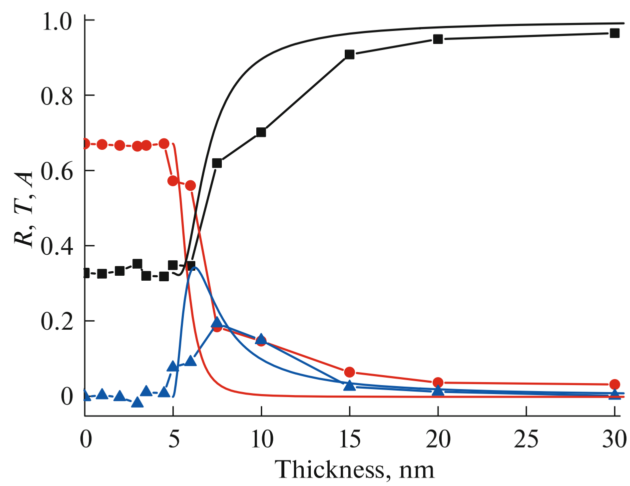

Fig. 6. Comparison of the optical coefficients (symbols) measured in the waveguide at a frequency of 10 GHz and (solid line) calculated for the copper conductivity bulk $\sigma_0 = 5.9 \times 10^7$ Sm/m. The calculated curves are shifted by 5 nm (the copper film thickness at which the continuous conducting layer begins to form).

respond to the calculated values also within 2%. However, the increase in the measured reflectance values with an increase in the thickness in the range of 5–15 nm is slower than what is given in the calculation data. The transmittances in this thicknesses range also do not correspond to the calculated values; one can observe a smoother increase in the absorption coefficient and a shift of its maximum to larger thicknesses by 2 nm.

The dependences of the phase shift for the reflected (φ_{11}) and transmitted (φ_{12}) waves with respect to the incident-wave phase on the film thickness are shown in Fig. 7. When the wave is reflected from the pure substrate, the phase shift depends on the frequency and varies from 140° to 147° with an increase in the frequency from 9 to 11 GHz. At a film thickness that does not exceed 5 nm, the measured phase-shift values fluctuate in the vicinity of the aforementioned values (Fig. 7a). A sharp phase jump is observed at the film thickness of 7.5 nm, when the conducting layer is formed, at which the phases of the reflected and incident waves are shifted by 180°. There is a transient mode of reflection from the film–substrate structure in the range of 5–7.5 nm. The calculations show that the film thickness of 1 nm is sufficient to provide the antiphase reflection. In accordance with the calculations, the transmitted-wave phase shift should decrease and levels off for film thicknesses exceeding 3 nm (Fig. 7b). However, the measurement results differ significantly from the theoretical calculation data. The transient mode for the measured transmitted-wave phase occurs in a much wider thickness range (from 5 to 15 nm). The leveling off is observed only for film thicknesses exceeding 20 nm. Note that

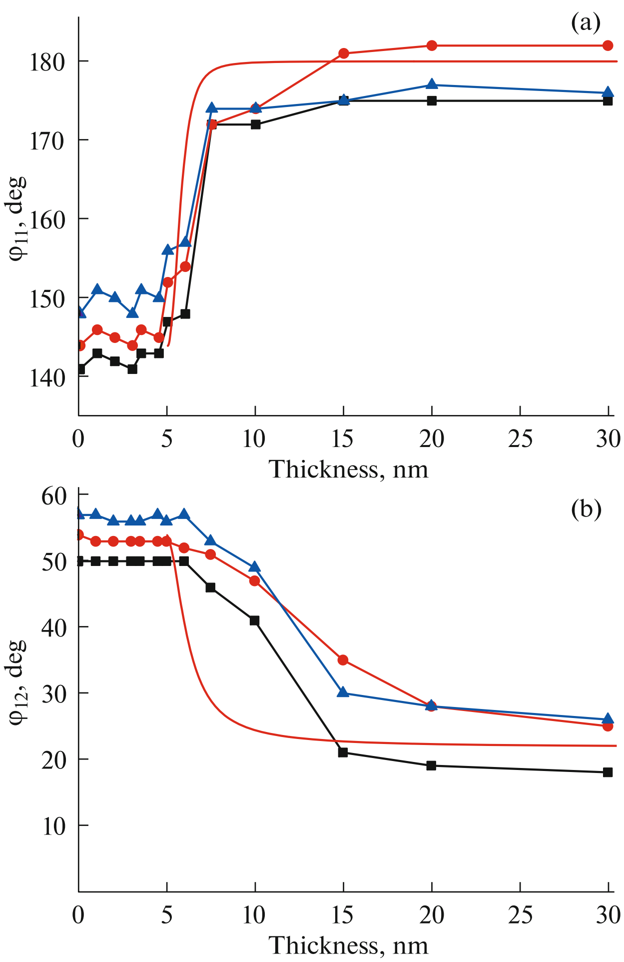

Fig. 7. Phase shifts of the (a) reflected and (b) transmitted waves with respect to the incident-wave phase depending on the film thickness. The measurement results at different frequencies are shown by symbols: (■) 9, (●) 10, and (▲) 11 GHz. The calculated data at a frequency of 10 GHz are shown by a solid line. The calculation curves are shifted by a thickness of 5 nm.

the phase measurements are fairly sensitive; therefore, they may serve as a tool for refining the film structure.

CONCLUSIONS

The results of measuring the reflectance and transmittance presented in Figs. 6 and 7 show that copper films with a thickness not exceeding 5 nm are almost transparent for radiation at frequencies of 9–11 GHz. Nanoscale copper films are very rapidly oxidized in air, as a result of which a stable oxide layer with a complex structure is formed [6, 7, 13]. The formation of the oxide layer occurs in several stages and depends strongly on the technological process of magnetron sputtering. In particular, copper films with a thickness up to 5 nm are almost completely (by 98.5%) oxidized due to storage in air. The films with a thickness of more than 5 nm exhibit metal properties: a conducting layer is formed, which reflects electromagnetic waves. However, as the inconsistency between the experimental and calculated optical coefficients shows, the structure of the conducting layer is inhomogeneous. In particular, it was shown in [13] that the percolation transition occurs at a thickness of 10–12 nm. The films with larger thicknesses exhibit purely metal properties, whereas the conductivity of the films with smaller thicknesses is determined to a larger degree by the film morphology. Here, intergranular contacts and grain structure and orientation play a decisive role [14, 15]. The presence of the oxide copper layer in the films several nanometers thick and inhomogeneities in the form of individual grains on the copper-film surface were mentioned in [16]. The film conductivity in the range of 5–12 nm should be calculated proceeding from the theory of effective medium [14, 15].

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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