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Effect of Thickness of the Dielectric Substrate on Absorbing and Antireflective Properties of Ultrathin Copper Films

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The dependence of optical coefficients of ultrathin copper films 2–30 nm thick on the substrate thickness has been studied. Films were fabricated on quartz substrates 4 mm thick, and the thickness of the substrates (6 and 8 mm) was varied by tightly pressing clean substrates with thicknesses of 2 and 4 mm to a 4 mm substrate with a film. The measurements were carried out in a waveguide in the frequency range 8.5–12.5 GHz in the TE_{10} mode for two film orientations with respect to direction of the incident wave. The dependences of the optical coefficients measured when the wave was incident from the side of the film and from the side of the substrate differ significantly. It is shown that the effect of anomalously high absorption of waves (more than 77%) by copper films no thicker than 10 nm is observed in a wide frequency band. The maximum absorption (77.5%) was obtained at frequency of 8.5 GHz when a wave was incident on a film 8.6 nm thick from the side of a 6-mm substrate. The effect of extremely low reflection (0.06%) was recorded for the first time when a wave of frequency 11.54 GHz was incident on a film 7.9 nm thick from the side of a 4-mm substrate. It is shown that the frequency range where the effect of minimal reflection was observed exceeds the antireflection band of a dielectric plate with half-wave resonance.

Keywords: ultrathin cooper films, quartz substrate, optical coefficients, waveguide measurements, microwave frequency range.

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Introduction

Metal films with a thickness of several nanometers are able to effectively absorb electromagnetic radiation in the microwave range [1]. In the review [2] it is theoretically shown that the maximum absorption coefficient of an ultrathin metal film without a substrate is 50%. The presence of a dielectric substrate has a significant effect on the optical coefficients of ultrathin films. This manifests itself primarily in a noticeable difference between the dependences of the optical coefficients measured when the wave is incident directly on the film and when the wave is incident on the film from the substrate side. We paid attention to this effect in our earlier studies. The maximum absorption coefficient of copper films [1] on a 2-mm quartz substrate did not exceed 0.25 in the case of wave incidence from the film side. However, when a wave was incident from the side of a 2-mm substrate onto a platinum film with similar parameters, the absorption coefficient increased to 0.45 [3]. These effects were observed for the films of several nanometers thick. One should expect an increase in the influence of substrates whih thickness is a quarter or half a wavelength at a certain frequency in the measured range.

Ultrathin metal films on transparent substrates are considered as a possible alternative to indium tin oxide for the manufacture of transparent electrodes for liquid crystal screens, organic light emitting diodes, and touch screens. In [4] it is reported about the creation of a flexible electrode based on a 6.5 nm thick silver-copper film enclosed between two dielectric layers of a transparent polymer with an absolute transmittance of $\sim 88.4\%$, which is even higher than the transmittance $\sim 88.1\%$ of the polymer substrate. Particular interest in thin-film absorbers of microwave radiation arose in connection with the planned introduction of 5G technology, where data transmission occurs in the frequency ranges 2.3–4.7 GHz and 24–54 GHz. In order to protect operators and sensitive devices from the influence of electromagnetic interference, it is proposed to use optically transparent coatings with a sufficiently large absorption of microwave radiation in a wide band. Coatings are being developed based on highly amorphous nanometer pyrolytic carbon (PyC) films, which consist of randomly oriented and intertwined graphene flakes with a typical size of several nanometers. Such coatings absorb up to 38% of incident radiation [5]. In a device based on an asymmetric Fabry-Perot resonator, a monolayer of graphene and a transparent ultrathin (8 nm) layer of doped silver [6] are used as an absorber of microwave radiation. Adjustment of the absorption peak is carried out by selecting the thickness of the layer of fused quartz located between the layers of graphene and silver.

The purpose of this work was to study the dependence of the optical coefficients of ultrathin copper films on the thickness of quartz substrates and to demonstrate the possibility of creating coatings with a high level of absorption and minimal reflection of microwave waves in a wide frequency band. In this case, the substrates were chosen so that their thickness was a quarter or a half of the wavelength at certain frequencies in the measured range. Copper films of a few nanometers thick are quite transparent in the visible region, so such coatings can serve as the basis for creating screens to protect against electromagnetic interference.

Materials and methods

Copper films were deposited in a vacuum setup with a pre-vacuum value no worse than $5 \cdot 10^{-6}$ mm Hg by thermal evaporation. The deposition was performed on the surface of 4 mm thick and 22.9×9.8 mm substrates, thoroughly cleaned by physicochemical methods and polished to optical grade roughness. All substrates were made of KU-1 grade optical quartz glass. Before the films were deposited, the substrates were annealed in a vacuum 10^{-6} mm Hg at a temperature of 250°C, after this they were cooled to the room temperature, at which the films were deposited. A sample of copper with a purity of 99.999% of the known mass was placed in a tungsten crucible and heated to the melting point. The evaporation time of the sample did not exceed 10 s. At such a deposition rate, the size of the islands, which are formed on the substrate surface at the initial stage of metal evaporation, decreased [7]. The crucible was placed at a distance of 10 cm from the substrate surface, which allowed to obtain the films of sufficiently uniform thickness. The film thickness was calculated from the weight of the sample, taking into account the relative position of the substrate and the crucible. To obtain a film with a thickness of 1.0 nm, it is necessary to take a sample weighing 1.24 mg. This ratio was obtained by measuring the thickness of films obtained by evaporating a sample of a known mass using KLA-Tencor Alpha-Step IQ stylus profilometer. To do this, the films with a thickness of 10 to 20 nm were deposited, and strips with a clear transition step from the substrate to the film were fabricated on their surface by lithography. The error in determining the film thickness by this method was 5%. In the measurements of the optical coefficients, films with a thickness of 4.0, 4.8, 5.8, 7.2, 7.9, 8.6, 10.5, 17.9, 26.4 nm were used. The films for which the measured optical coefficients differed from those for a clean substrate are shown in Fig. 1, *a*. The optical coefficients of ultrathin copper films were measured in the duct of a rectangular waveguide in the frequency range 8.5–12.5 GHz for two film orientations with respect to the incident wave direction (Fig. 1, *b*). In the fq (film-quartz) orientation the wave was incident directly on the film surface, while in the qf (quartz-film) orientation the wave was incident on the film after passing through the quartz substrate. The measurement scheme was made absolutely symmetrical with respect to the channels of the vector analyzer: the substrate holder with the film was placed between two waveguide-to-coax adapters (WCA), which were connected to channels 1 and 2 of the ZVA-24 vector network analyzer. When the film was on the channel 1 side, the measured amplitude scattering parameters S_{11} and S_{12} corresponded to the amplitude reflection and transmission coefficients for the fq orientation, and S_{22} and S_{21} — to amplitude reflection and transmission coefficients for the qf orientation. The calibration of the measuring path was carried out in the total reflection mode, when a polished copper plate, which completely reflects microwave radiation, was installed in place of the substrate holder, and in the full transmission mode, when the holder was installed without a substrate, i.e., in the absence of any inhomogeneities in the path. This calibration ensured good agreement between the measured and calculated values of the amplitude and phase of the optical coefficients of pure quartz substrates. The energy coefficients of reflection R, transmission T and absorption A were calculated using the formulas:

$$R_{\text{fq}} = S_{11}^2,\ R_{\text{qf}} = S_{22}^2, T_{\text{fq}} = S_{12}^2,\ T_{\text{qf}} = S_{21}^2,$$

$$A_{\text{fq}} = 1 - R_{\text{fq}} - T_{\text{fq}},\ A_{\text{qf}} = 1 - R_{\text{qf}} - T_{\text{qf}}. \qquad (1)$$

The phases of the optical coefficients for the corresponding orientations corresponded to the measured phases of the scattering parameters S_{ij}. To measure the dependences of the optical coefficients of copper films on the thickness of the substrate, it was proposed to deposit films on substrates of only one thickness; in our case, substrates with a thickness of 4 mm were chosen. The substrate thickness was varied by pressing firmly against a 4 mm substrate with a film of a clean substrate from the side where the film was absent. We had at our disposal 2 and 4 mm substrates, as a result the measurements were carried out both with a 4 mm substrate and with their combinations $4 + 2 = 6$ mm and $4 + 4 = 8$ mm. The advantage of the proposed technique was the use of the same films, since it is quite difficult to deposit completely identical films of nanometer thickness. To confirm the legitimacy of using such a technique, we measured the reflection and transmission coefficients of a clean substrate with a thickness of 4 mm and a combination of two 2-mm substrates, which coincided within 2%.

Measurement results

Measurements of optical coefficients of clean substrates and experimental determination of dielectric permittivity of quartz glass

At the first stage, test measurements of the reflection and transmission coefficients of clean substrates were

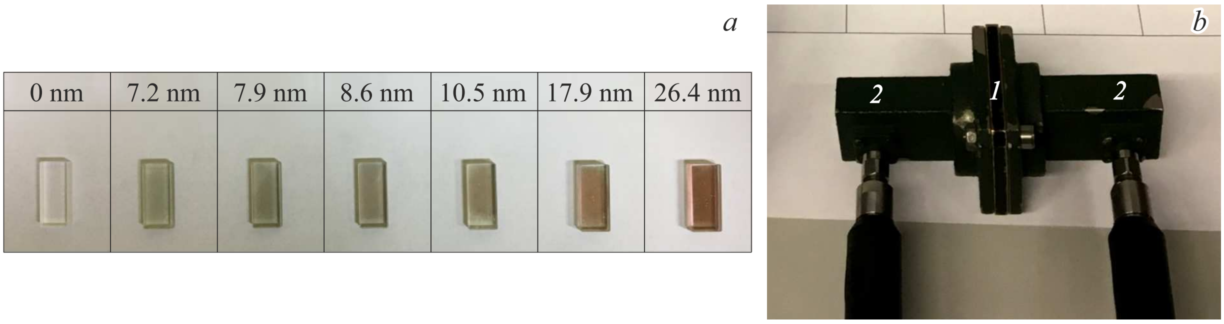

Figure 1. Copper films of various thicknesses on substrates (*a*) and the waveguide part of the experimental setup (*b*): *1* — measuring film holder, *2* — waveguide-to-coax adapters (WCA).

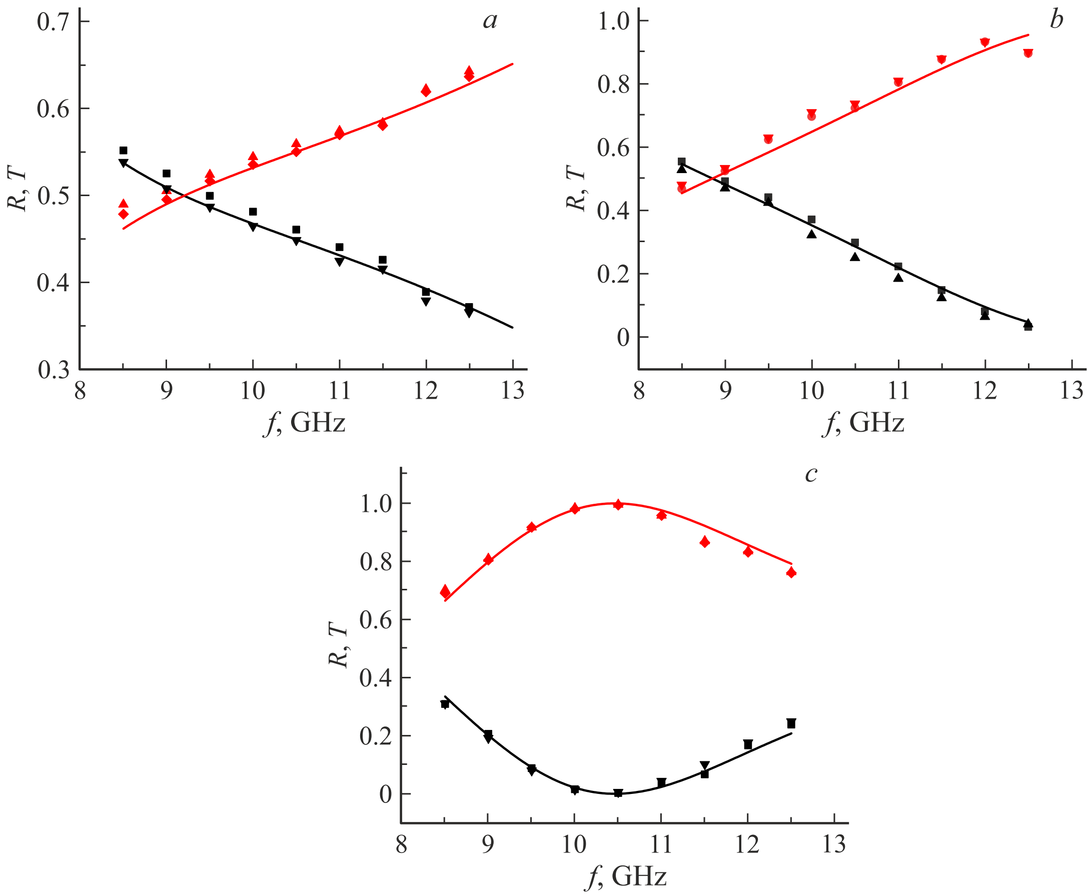

Figure 2. Reflectance R_{11} (■), R_{22} (▼) and transmission coefficients T_{12} (♦), T_{21} (▲), measured for substrates 4 mm (*a*), 6 mm (combination 4 + 2 mm) (*b*) and 8 mm (4 + 4 mm) thick (*c*). The lines show the reflection and transmission coefficients calculated for $\varepsilon = 3.6$.

carried out in the frequency range 8.5–12.5 GHz. In the measurements, we used 2 and 4 mm substrates, as well as their combinations 4 + 2 mm and 4 + 4 mm, when a pair of substrates tightly pressed against each other was inserted into the holder. Since the measurement scheme is symmetrical with respect to channels 1 and 2, the reflection coefficients for the wave incident from channel 1 (R_{11}) and from channel 2 (R_{22}) almost coincide (Fig. 2). A similar statement is also true for the transmission coefficients T_{12} and T_{21}. The measured values of the optical coefficients were compared with the results of calculations using known formulas [8] with allowance for waveguide propagation. The permittivity of quartz glass ε was varied so that the root-mean-square deviation of the calculated values of optical coefficients was minimal for all combinations of substrates. The result was $\varepsilon = 3.6$, which is slightly different from the value ($\varepsilon = 3.8$) given in [9]. A substrate with a thickness of 8 mm (at $\varepsilon = 3.6$) is half-wave at a frequency of 10.46 GHz;

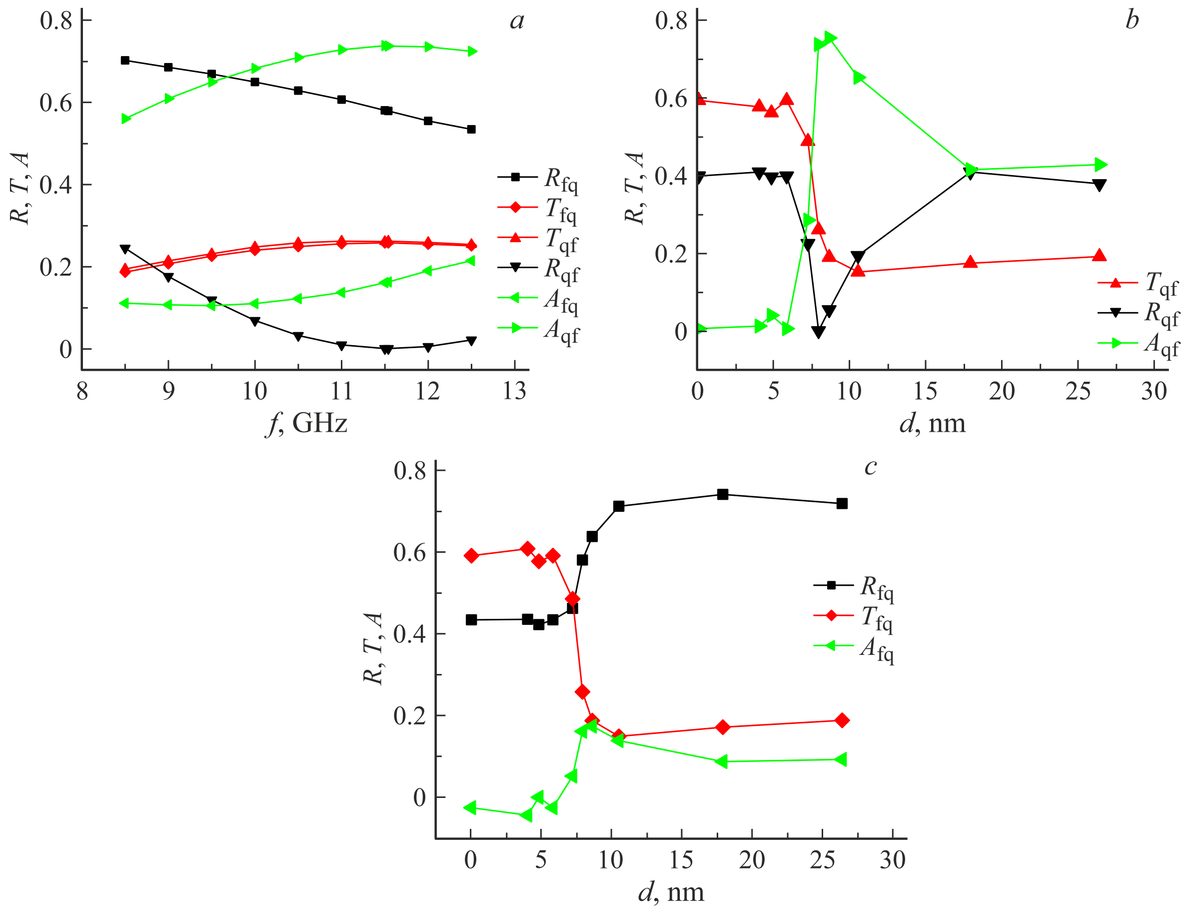

Figure 3. Frequency dependences of the optical coefficients of a 7.9 nm film on a 4-mm substrate, measured with a wave incident from the side of the film (R_{fq} (■), T_{fq} (♦), A_{fq} (◄)) and from the side of the quartz substrate (R_{qf} (▼), T_{qf} (▲), A_{qf} (►)) (*a*). R_{fq} (▼), T_{qf} (▲), A_{qf} (►) (*b*) and R_{fq} (■), T_{fq} (♦), A_{fq} (◄) (*c*) on the film thickness *d* on a 4 mm substrate, measured at a frequency of 11.5 GHz. Symbols are connected by lines for clarity.

therefore, at the indicated frequency, a reflection minimum is observed, and the transmittance is 1 (Fig. 2, *c*). Good agreement over the entire measured frequency range of the measured and calculated values of the optical coefficients of clean substrates and their combinations showed that the calibration of the measuring path was performed quite accurately, and also once again demonstrated the legitimacy of using substrate combinations to vary their thicknesses. In the future, the obtained value ε is planned to be used for numerical calculations of the complex optical coefficients of copper films on substrates.

Measurements of optical coefficients of copper films on the substrates of different thickness

Figure 3, *a* shows the frequency dependences of the optical coefficients R, T and A of the 7.9 nm film on a 4-mm substrate, measured when the wave was incident both from the side film (fq), and from the side of the quartz substrate (qf). The transmission coefficients, due to the symmetry of the measurement scheme, coincide and practically do not depend on the frequency, remaining approximately at the level of 0.2–0.26. The reflection coefficient R_{fq} decreases monotonically from 0.7 ($f = 8.5$ GHz) to 0.53 ($f = 12.5$ GHz), while the absorption coefficient A_{fq} accordingly smoothly increases from 0.11 ($f = 8.5$ GHz) to 0.21 ($f = 12.5$ GHz). The reflection coefficient in the case of wave incidence from the side of a 4-mm substrate decreases from 0.24, reaches almost zero ($6.8 \cdot 10^{-4}$) at a frequency of 11.54 GHz, and then increases to 0.02 ($f = 12.5$ GHz). The absorption coefficient A_{qf} increases from 0.56 ($f = 8.5$ GHz), reaches a maximum of 0.73 ($f = 11.54$ GHz) and decreases to 0.72 at the edge of the range ($f = 12.5$ GHz). The frequency range where the absorption maximum $A_{qf} > 0.72$ and the reflection minimum $R_{qf} < 0.03$ is observed is about 2 GHz.

The dependences of the coefficients R_{qf}, T_{qf} and A_{qf} on the film thickness on a 4-mm substrate, measured at a frequency of 11.5 GHz, are shown in Fig. 3, *b*. For the films with the thickness of up to 6 nm, a continuous metal layer has not yet formed, and their optical coefficients practically do not differ from the values measured for a clean substrate.

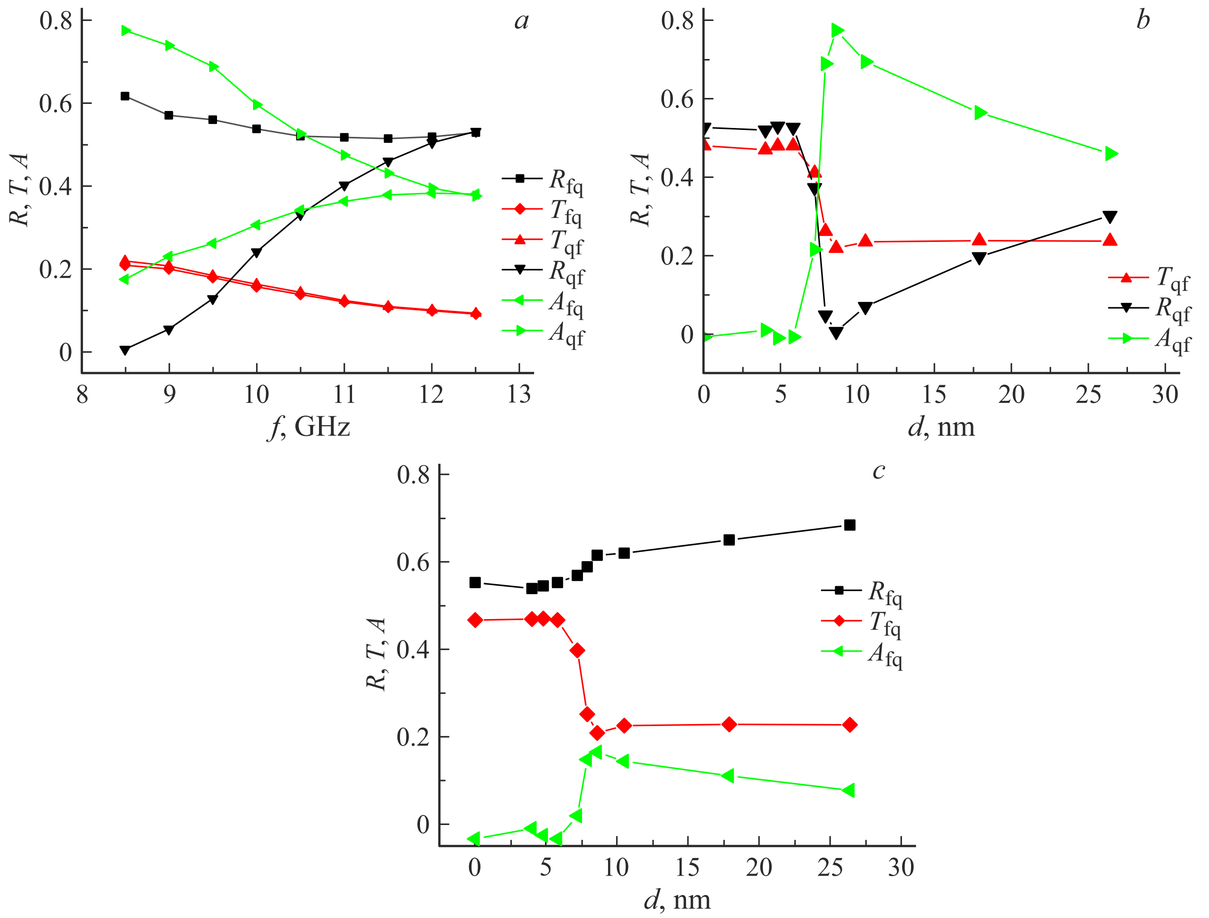

Figure 4. Frequency dependences of the optical coefficients of the 8.6 nm film on a 6-mm substrate (4 + 2 combination), measured with a wave incident from the side of the film (R_{fq} (■), T_{fq} (♦), A_{fq} (◄)) and from the side of the quartz substrate (R_{qf} (▼), T_{qf} (▲) and A_{qf} (►)) (*a*) Coefficient dependencies (R_{qf} (▼), T_{qf} (▲) and A_{qf} (►)) (*b*) and (R_{fq} (■), T_{fq} (♦), A_{fq} (◄) (*c*) on the film thickness *d* on a 6 mm substrate, measured at a frequency of 8.5 GHz. Symbols are connected by lines for clarity.

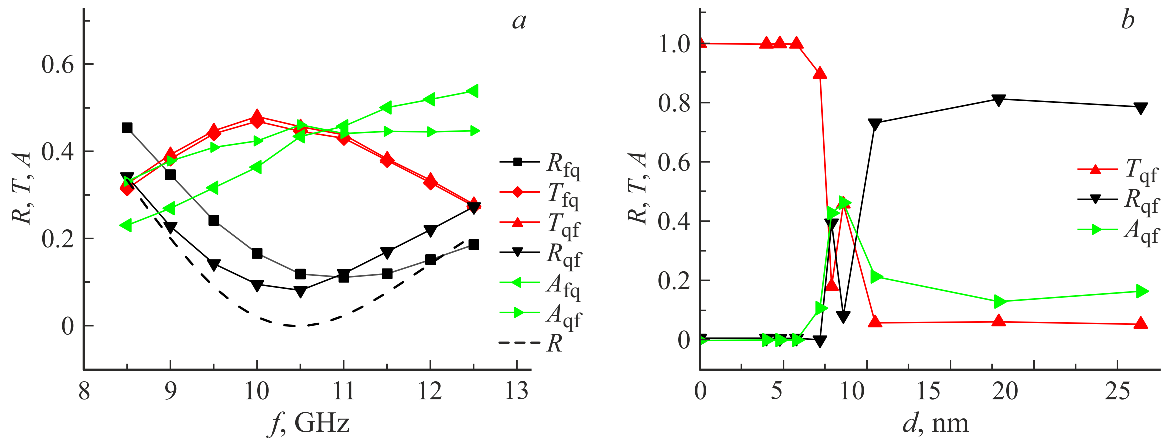

Figure 5. Frequency dependences of coefficients *R*, *T*, *A*, measured for 8.6 nm film on 8-mm substrate (combination 4 + 4 mm). The dashed line shows the calculated dependence of the reflection coefficient of a clean 8-mm substrate (*a*). Dependences of the coefficients R_{qf}, T_{qf} and A_{qf} on the film thickness, measured at a frequency of 10.5 GHz (*b*).

In our measurements the minimum thickness at which the films began to exhibit metallic properties was 7.2 nm. In the region 7.2–7.9 nm, a sharp decrease in R_{qf} is observed, after which the region of thicknesses begins, at which the reflection increases and the transmission decreases. For the films thicker than 18 nm, the coefficients R_{qf}, T_{qf}

reach an approximately constant level. The absorption coefficient has a maximum $A_{\mathrm{qf}} = 0.76$ for a film with a thickness of 8.6 nm, after which it decreases and reaches an approximately constant level for the films with a thickness of more than 18 nm. When the wave is incident from the film side, the dependences of the optical coefficients on the thickness do not have any features (Fig. 3, c). The absorption coefficient has a weakly pronounced maximum ($A_{\mathrm{fq}} = 0.17$) at a film thickness of 8.6 nm.

An increase in the substrate thickness to 6 mm $(4 + 2)$ leads to a noticeable change in the optical coefficients (Fig. 4, a, b). The transmission coefficients ($T_{\mathrm{qf}} \approx T_{\mathrm{fq}}$) of the 8.6 nm film decrease monotonically with the increasing frequency from $T_{\mathrm{qf}} = 0.22$ ($f = 8.5$ GHz) to 0.09 ($f = 12.5$ GHz). The reflection coefficient R_{fq} varies within limits not exceeding 20% ($0.53 < R_{\mathrm{fq}} < 0.62$). The reflection coefficient when the wave is incident from the side of the substrate R_{qf} has a minimum of $6.4 \cdot 10^{-3}$ at the edge of the range ($f = 8.5$ GHz), then it rapidly increases to frequency 12.5 GHz is compared with R_{fq}. The absorption coefficient A_{qf} at the frequency $f = 8.5$ GHz has a value of 0.775, which is the absolute maximum for the absorption recorded in all our measurements. As the frequency increases, A_{qf} decreases, and at the frequency $f = 12.5$ GHz it is compared with A_{fq}. Figure 4, b shows the dependences of the coefficients R_{qf}, T_{qf} and A_{qf} on the thickness films on a 6-mm substrate, measured at a frequency of 8.5 GHz. At this frequency, a reflection minimum ($R_{\mathrm{qf}} = 6.4 \cdot 10^{-3}$) and an absorption maximum ($A_{\mathrm{qf}} = 0.775$) were observed for the 8.6 nm film. The nature of the dependences of the optical coefficients on the film thickness on 4 and 6 mm substrates is almost identical (Fig. 3, b and 4, b). Small differences in the coefficients for films on 6 mm substrates are observed in numerical values and in the absence of stabilization of the coefficients R_{qf}, T_{qf} for films thicker than 18 nm.

The minimum value of the reflection coefficient ($R_{\mathrm{qf}} = 0.08$) for films on an 8-mm substrate was observed at a frequency of 10.5 GHz and a film thickness of 8.6 nm when the wave was incident from the side of the substrate (Fig. 5, a). This frequency is near the half-wave resonance (10.46 GHz) for a clean 8-mm substrate. The measured reflection coefficient of a clean substrate at this frequency was $2.5 \cdot 10^{-3}$.

A feature of the 8.6 nm film on an 8-mm substrate is a slight difference in the reflection coefficients when the wave is incident both from the side of the film R_{fq} and from the side of the substrate R_{qf}, as well as their relatively small value in the entire range of measured frequencies. The maximum absorption coefficient ($A_{\mathrm{fq}} = 0.54$) was registered at a frequency of 12.5 GHz when a wave was incident on a film with a thickness of 8.6 nm. At a frequency of 10.5 GHz (Fig. 5, b) for films whose thickness exceeds 8.6 nm, the reflection coefficient is maximum ($R_{\mathrm{qf}} \approx R_{\mathrm{fq}} \approx 0.8$), the transmittance is minimal ($T_{\mathrm{qf}} \approx T_{\mathrm{fq}} \approx 0.06$), and the absorption coefficient does not exceed 0.2. Note that the dependences of the coefficients on the film thickness at the indicated frequency are almost identical both for the wave incident from the side of the film and from the side of the substrate.

Conclusion

It has been experimentally shown that the effect of anomalously high absorption of microwaves by ultrathin metal films is observed in a wide frequency band. The maximum absorption ($A_{\mathrm{qf}} = 0.775$) was recorded at a frequency of 8.5 GHz in the 8.6 nm film deposited on a 6-mm substrate. A slightly lower absorption ($A_{\mathrm{qf}} = 0.74$) was measured in the 7.9 nm film on a 4 mm substrate at a frequency of 11.5 GHz. In this case, the absorption coefficient of this film is practically independent of the frequency in the entire measured band 8.5–12.5 GHz and averages 0.6. Note that the effect strongly depends on the orientation of the film relative to the incident radiation. The absorption values indicated above were obtained when the wave was incident on the film from the substrates side. For the 8 mm substrate the maximum absorption coefficient ($A_{\mathrm{fq}} = 0.54$) was recorded at a frequency of 12.5 GHz when the wave was directly incident on the 8.6 nm film. The presence of ultrathin metal films significantly affects the radiation reflection coefficient, while the frequency band of such an antireflection effect can be wider than that of a half-wave dielectric plate. It should be specially emphasized that the high absorption level (coefficient A_{qf}) of the 7.9 and 8.6 nm films on a 4-mm substrate is followed by a significant decrease in the reflection coefficient R_{qf} (Fig. 3). This fact is of fundamental importance for the creation of protective electromagnetic screens, since simultaneously with absorption, the level of spurious reflections decreases and the effect of the appearance of bright glare spots is minimized. In this case, the films with thicknesses up to 10 nm (Fig. 1, a) transmit radiation well in the optical range, and this allows to use them for optically transparent screens.

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Conflict of interest

The authors declare that they have no conflict of interest.

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