# Optical and electrical properties of ultrathin metallic films

L. A. Kuzik, Yu. E. Petrov, F. A. Pudonin, and V. A. Yakovlev

*Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow Province, Russia*

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We have made a comprehensive investigation of the optical and electrical properties of ultrathin Nb films (2–72 Å thick) and Cu films (1–42 Å thick), using transmission, reflection, and frustrated total internal reflection spectra as well as dc conductivity measurements. The properties of the films were found to be oscillatory functions of the film thickness. The period of the oscillations is different for different metals and both substrate and temperature independent. It can be inferred that the oscillations are associated with the quantum size effect.

Low-dimensional objects are increasingly attracting attention. Such objects exhibit unusual properties which are different from the bulk properties of the original materials. Investigations of such objects are of great fundamental importance, because such studies will shed light on the behavior of the electron density of states of such thin layers as well as on the optical and electrical properties of low-dimensional objects, which, in turn, is important for the development of coatings with new predictable properties.

Ultrathin metal films are low-dimensional objects. The study of such samples for metals with good conductivity became possible only with the use of rf sputtering for preparing the films. This method makes it possible to obtain $\sim 10^{-12}$ m thick mirror-smooth continuous films of metals.[1]

## 1. SAMPLE PREPARATION

In this work we investigated several series of samples of niobium and copper thin films on crystalline quartz and silicon substrates. Quartz substrates with dimensions $15\times 15\times 3$ mm$^3$ were prepared from crystalline quartz (Qu); the optical axis was oriented along one of the long edges. Silicon (Si) substrates were prepared from 0.4 mm thick crystalline wafers used for microcircuits; the top face had [111] orientation, and the substrates had an area of 0.5–1.5 cm$^2$. The films were deposited by rf sputtering with the SPUTRON II apparatus. The series of metal films investigated in this work are presented in Table I. The film thicknesses were monitored using the sputtering time. Immediately after deposition the metal films were coated with a 40–50 Å thick protective film of silicon in order to protect the metal film from oxidation and contamination. Films so protected retained their properties for months.

## 2. OPTICAL MEASUREMENTS AT ROOM TEMPERATURE

The reflection and transmission spectra were obtained, with the help of a Michelson-110 (BOMEM) Fourier spectrometer, for all films in the transmission range of the substrates—2500–5000 cm$^{-1}$ on quartz and 500–5000 cm$^{-1}$ on silicon. The transmission spectra of the series No. 2 niobium films are displayed in Fig. 1. A characteristic feature of the transmission and reflection spectra for all series is that when the thickness changes uniformly, the reflection and transmission of the films change nonuniformly as a function of the thickness.

The optical constants of very thin films cannot be determined uniquely from the transmission and reflection spectra.[2] The transmission and reflection coefficients of the samples in the transmission range of the substrates are insensitive to the real part of the film permittivity. However, the imaginary part of the film permittivity can be estimated from the reflectance and transmission spectra with the help of approximate formulas. For normal incidence on a film with permittivity $\varepsilon_2$ and thickness $d$ on a substrate with permittivity $\varepsilon_3$ and thickness $D$ and with $|4\pi\nu\varepsilon_2 d| \ll 1$ $(2\pi\nu c=\omega)$, we have in the transmission range of the substrate $(4\pi\nu D\,\mathrm{Im}\,\varepsilon_3 \ll 1)$

$$\mathrm{Im}\,\varepsilon_2 \simeq \frac{R-R_0}{4\pi\nu d R_0}\left\{\frac{1+2R_s}{(\varepsilon_3-1)(1+R_s)}-\frac{1-R_s}{\sqrt{\varepsilon_3}+1}\right\}^{-1}$$
$$\simeq \frac{T-T_0}{4\pi\nu d T_0}\left\{\frac{2R_s^2}{(\varepsilon_3-1)(1-R_s^2)}-\frac{1}{\sqrt{\varepsilon_3}+1}\right\}^{-1}, \quad (1)$$

where $R_0$ and $R$ are the reflection coefficients of the substrate without and with the film, respectively; $T_0$ and $T$ are the transmission coefficients of the substrate without and with the film, respectively; and, $R_s=R_0/(2-R_0)$ is the reflection coefficient of one surface of the substrate.

The values of $\mathrm{Im}\,\varepsilon_2$ calculated for each sample from the reflection and transmission spectra were within 5% of one another. Plots of $\mathrm{Im}\,\varepsilon_2$ at 3000 cm$^{-1}$ as a function of the film thickness are displayed for a series of samples in Fig. 2 for niobium and Fig. 3 for copper. The imaginary parts of the permittivity for the same film thickness are different in different series, but the character of the curves is the same. A common feature of all curves is their oscillatory form. The average period of the oscillations is 6 Å for niobium films and 2 Å for copper films. If the imaginary part of the permittivity is known, then the conductivity at optical frequencies can be calculated from the formula

$$\sigma(\nu)=\frac{\mathrm{Im}\,\varepsilon}{4\pi\nu}.$$

TABLE I.

| Series No. | Metal | $d_{\min}$, Å | $d_{\max}$, Å | $\Delta d$, Å | Substrate |
|---|---|---|---|---|---|
| 1 | Nb | 1.5 | 10.5 | 1.5 | Qu |
| 2 | Nb | 2.0 | 20.0 | 2.0 | Qu |
| 3 | Nb | 3.0 | 27.5 | 1.5 | Qu |
| 4 | Nb | 3.0 | 72.0 | 1.5 | Si |
| 5 | Cu | 3.0 | 42.0 | 1.0 | Si |
| 6 | Cu | 2.5 | 21.0 | 0.5 | Si |

It can thus be concluded that for the experimental films, the optical conductivity at all measured frequencies is a periodic function of the thickness.

Periodicity of the optical properties can also be seen in other optical measurements—in particular, the surface polariton spectra of quartz. The frustrated total internal reflection spectra were measured for the No. 2 niobium films. The surface polariton spectra of crystalline quartz, altered by the presence of a film on the quartz surface, are displayed in Fig. 4. The frequency and width of the surface polariton line of quartz as a function of the thickness of the niobium film are displayed in Fig. 5. The curves are nonmonotonic with a period of 6 Å; this also indicates that the properties of the niobium films are periodic functions of the thickness.

## 3. MEASUREMENT OF DC CONDUCTIVITY

Periodicity of the properties of niobium films is seen not only in optical measurements but also in measurements of the dc conductivity. The dc conductivity was measured for samples from series Nos. 2 and 3 niobium films. The measurements were performed by the four-contact method.[3] Four needle probes were arranged near the boundaries along the perimeter of the film. Direct current was passed through one pair of neighboring contacts and the voltage across the other pair of contacts was measured. Since the films were deposited on quartz, which is a good insulator, the dc conductivity is determined only by the metal film on the quartz surface. Due to its small thickness, the protective silicon film has no effect on the measurements.

All films thicker than 3 Å have an ohmic voltage-current curve; this confirms that the films are continuous. When the position of the probes was changed, the conductivity changed by less than 1%; this indicates that the spatial uniformity of the films is good. Figure 6 displays plots of the dc conductivity versus the film thickness for series Nos. 2 and 3. The conductivity oscillates as a function of the thickness, the period being the same as in optical measurements (6 Å). The dc conductivity of the silicon substrates was not measured, since the conductivity of silicon is fairly high, which makes it impossible to measure the contribution of the very thin metal film to the conductivity.

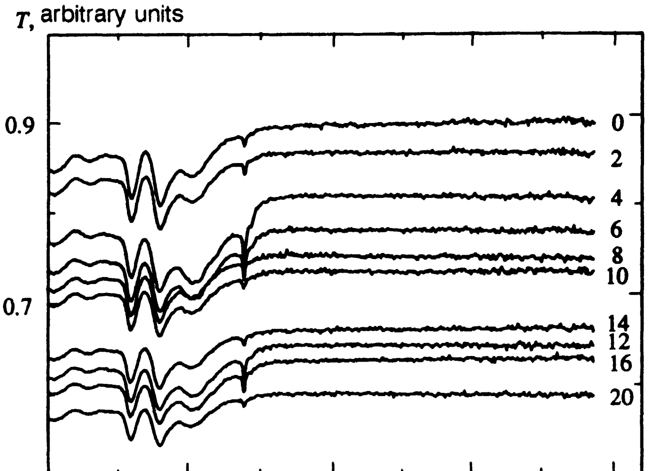

FIG. 1. Transmission spectra of series No. 2 niobium films (the film thickness in Å is indicated near the curves).

Thus both the dc and optical-frequency conductivity are periodic functions of the film thickness.

## 4. DEVIATIONS FROM PERIODIC BEHAVIOR

Additional aperiodic modulation, superposed on the periodic behavior, is seen in each series. It can be attributed to the technology employed for preparing the films. Each series was prepared in stages. Five to seven samples were prepared in each sputtering cycle. The properties of the films are very sensitive to the conditions during sputtering, and since it is very difficult to maintain constant conditions from one cycle to another, the properties of the films can vary. This affects primarily the specularity of the films, which should result in a decrease of the amplitude of the oscillations.[4] The small change in the period of the oscillations could be caused by the uncertainty in the film thick-

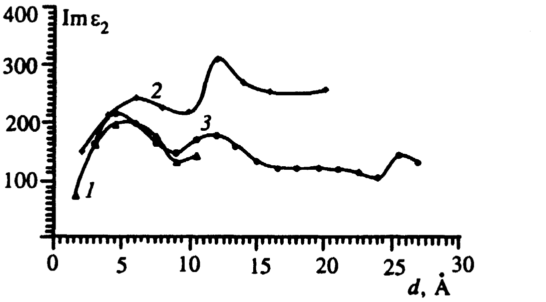

FIG. 2. Imaginary part of the permittivity at 3000 cm$^{-1}$ versus the thickness for different series of samples of niobium films: *1*—series No. 1; *2*—series No. 2; *3*—series No. 3.

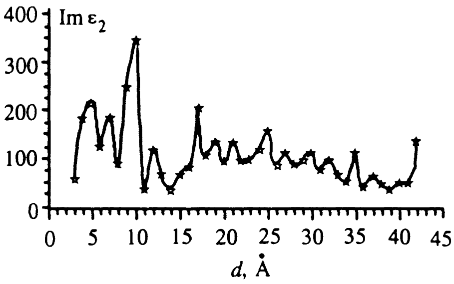

FIG. 3. Imaginary part of the permittivity at 2000 cm$^{-1}$ versus the thickness for series No. 5 copper films.

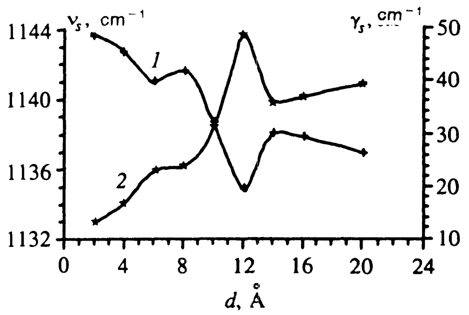

FIG. 5. Frequency $\nu_s$ (curve *1*) and width $\gamma_s$ (curve *2*) of surface polariton in quartz versus the thickness of a niobium film.

ness determined from the time, which depended on the sputtering rate. The sputtering rate was held constant while preparing a given series of samples, and depended on the step of the change in thickness: the smaller the step, the lower the sputtering rate. In all series, the film thickness was in error by less than 0.3 Å.

## 5. LOW-TEMPERATURE MEASUREMENTS

In order to determine possible reasons for the oscillatory character of the physical quantities, the conductivity and reflection spectra of the niobium films were measured at low temperature. Plots of the dc conductivity versus the thickness are displayed in Fig. 6 for series Nos. 2 and 3.

The effect of temperature on the optical properties of niobium films was studied in the reflection spectra recorded for series No. 3 samples in the range 450–2200 cm$^{-1}$. The room temperature reflection spectra of quartz coated with thin niobium films were measured with an FS-02 Fourier spectrometer. Some spectra are displayed in Fig. 7a. In order to measure the reflection coefficients at 10 K, the samples were placed in turn into a continuous-flow liquid helium cryostat. The spectra of the samples at 10 K were measured with an IFS-114 Fourier spectrometer. Some spectra are displayed in Fig. 7b.

To calculate the optical constants of the films, it is first necessary to determine the optical constants of the substrate, i.e., the quartz. A dispersion analysis of the spectra of pure quartz was performed, the parameters of the Lorentzian oscillators were found, and the permittivity was computed.

The optical constants of very thin films cannot be calculated by means of dispersion analysis.[5] However, the imaginary part of the film permittivity can be approximated in regions where the absorption by the substrate is weak and the substrate is opaque due to the large thickness $D$ ($4\pi\nu D \operatorname{Im} \varepsilon_3 \gg 1$):

$$R \approx R_0 \left\{ 1 + 8\pi\nu d \operatorname{Im}\left( \frac{\varepsilon_2 - 1}{\varepsilon_3 - 1} \right) \right\}. \tag{2}$$

The results are displayed in Fig. 8. By comparing the curves of $\operatorname{Im} \varepsilon_2$ for the films at the same frequency as a function of thickness for different temperatures, it can be shown that the period and amplitude of the oscillations are independent of the temperature.

Identical conclusions can be drawn from measurements of the dc conductivity of niobium films at room temperature and at the temperature of liquid helium (see Fig. 6).

Once the conductivity of films at different temperatures is known, the resistance of the films can be calculated as a function of frequency for these temperatures, after

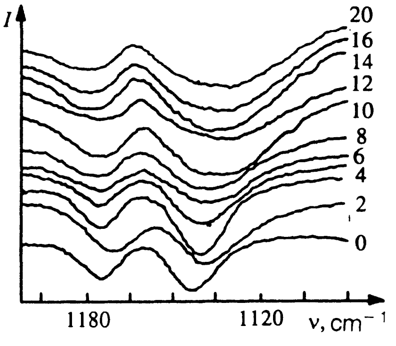

FIG. 4. Frustrated-total-internal-reflection spectra of surface polaritons of quartz coated with niobium films (series No. 2) of different thickness (indicated in Å near the curves).

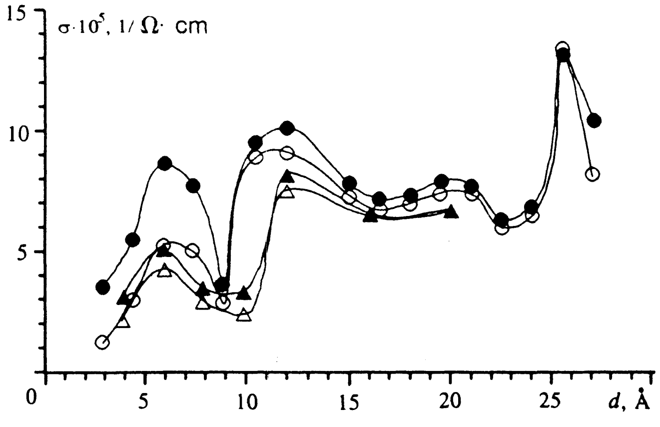

FIG. 6. DC conductivity of niobium films of series No. 2 (triangles) and No. 3 (circles) versus film thickness at room temperature (dark symbols) and liquid-helium temperature (light-colored symbols).

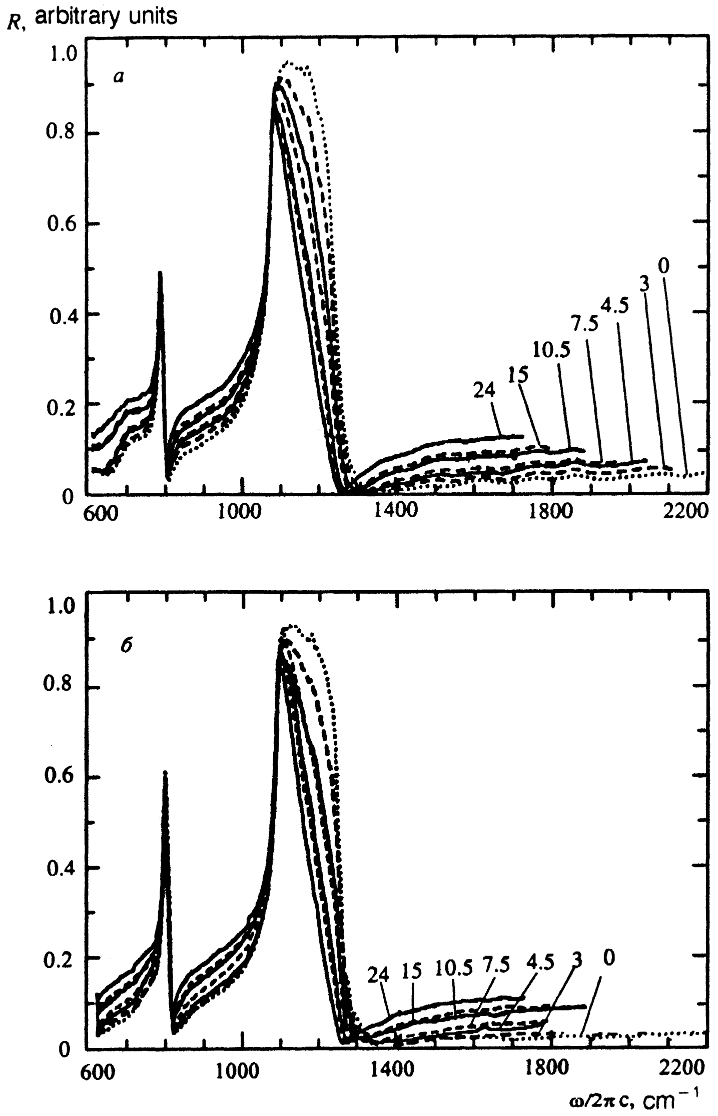

FIG. 7. Reflection spectra of some series No. 3 niobium films at room temperature (a) and at 10 K (b) for different film thicknesses, indicated (in Å) near the curves (E||c).

which the temperature-averaged temperature coefficient of resistance (TCR) can be calculated at different frequencies. It was found that the TCR is negative for dc and at frequencies below 1000 $\mathrm{cm}^{-1}$ (with the exception of a 25.5-Å film, for which the TCR is positive at all frequencies), and positive for all films at frequencies above 1000 $\mathrm{cm}^{-1}$.

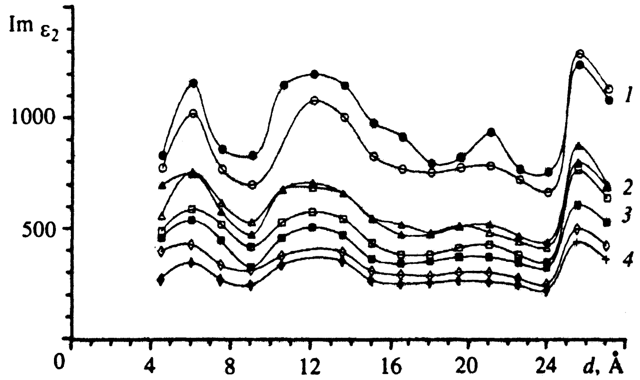

FIG. 8. Im $\varepsilon_2$ of niobium films versus film thickness at different temperatures and for different frequencies (dark-colored symbols—room temperature; light-colored symbols—10 K): $v = 650\ \mathrm{cm}^{-1}$ (*1*), $970\ \mathrm{cm}^{-1}$ (*2*), $1680\ \mathrm{cm}^{-1}$ (*3*), and $2060\ \mathrm{cm}^{-1}$ (*4*).

The resistance of bulk metals usually increases monotonically with temperature due to increasing electron-phonon and electron-electron scattering,[6] and their TCR is therefore positive. A negative TCR can be observed in thin films either because the films have an island structure or because they are contaminated.[7] This can be explained by electron localization and tunneling, which increase the resistance at low temperatures.

The films can thus be represented as flat regions of metal with dimensions of the order of $v_F/vc \sim 100$–$200$ Å, where $v_F$ is the electron Fermi velocity in niobium[8] and $v$ is the frequency at which the TCR changes sign. These regions are separated by boundaries formed by defects and contaminants. The conductivity of the films and the negative sign of the real part of the permittivity are determined primarily by the regions of metal and not by the boundaries between the metallic regions. This agrees with the analysis of a film in the effective-medium approximation.[9] Due to the presence of the boundaries, the low-frequency temperature dependence of the conductivity is different from that typical of metals.

## 6. DISCUSSION

The period of the optical and electrical properties is comparable to atomic dimensions. This suggests that the oscillations are associated with the quantum size effect. An ultrathin metal film with a thickness of the order of a nanometer can be viewed as a quantum well with infinitely high walls and width equal to the thickness of the film. In such a system, the momentum of the free carriers is quantized, and this results in periodic variation of the properties of the films. Sandomirskii developed a theory of the quantum size effect for semimetals.[10] According to this theory, the dc conductivity is a periodic function of thickness, with period equal to half the Fermi wavelength. Sandomirskii's theory has been confirmed experimentally for thin films of bismuth,[11,12] antimony,[13] and tin.[14]

The quantum size effect could not be observed previously for most highly conductive metals due to the difficulty in preparing continuous films with a thickness of $\sim 10^{-12}$ m. Radio frequency sputtering has made it possible to obtain high-quality mirror-smooth films with a reproducible quantum size effect for each series of samples. For niobium and copper, the period of the properties of the films as a function of thickness is of the same order of magnitude as the computed value of the Fermi wavelength.[8,15]

Sandomirskii's theory also implies that the period of the conductivity as a function of the thickness is temperature-independent. This temperature independence is associated with the quantized nature of the momentum of electrons in a potential well. The temperature independence of the amplitude of the oscillations is explained by the fact that near the Fermi level, the splitting of the quantum levels in a quantum well is of the order of several electron volts,[16] which is significantly greater than $kT$.

Thus, Sandomirskii's theory qualitatively explains the results. A more complete quantitative description, however, requires a more detailed theory and additional experimental investigations of thin films of different metals.

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