Optica Applicata, Vol. XV, No. 2, 1985

Optical anomalies of metallic island films*

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Optical properties of island metallic films have been reported in this paper. Experimental results illustrating optical anomalies in silver-, gold- and aluminium films have been reviewed. A modified Maxwell-Garnett- and Hampe-Shklyarevskii theories have been presented which are used for explanation of optical properties of island films. The above theories have been here employed for aluminium island films in order to compare both of them.

Optical properties of very thin and island films differ from those of bulk media or continuous thick films. The latter may be described basing on the classical Drude-Lorentz- and interband-transition quantum theories [1-4].

Interaction between electromagnetic wave and medium may lead to the free-electron absorption in bands filled incompletely and to the interband absorption (quantum one).

Optical medium properties are described with the dielectric permittivity

$$\hat{\varepsilon} = \varepsilon_1 - i\varepsilon_2 = (n-ik)^2 \tag{1}$$

where ε_1, ε_2 are the real and imaginary parts of the permittivity, respectively, n – refractive index, k – extinction coefficient. This value can be described for classical and quantum interactions in the analogous way.

N atoms are considered in the unit volume and N_j denotes density of electrons connected with a resonance frequency ω_j; the dielectric permittivity in case of an interaction between the wave and this system takes the form

$$\hat{\varepsilon} = 1 + \frac{4\pi e^2}{m} \sum_j \frac{N_j}{(\omega_j^2-\omega^2)-i\gamma_j\omega} \tag{2}$$

where γ_j is a factor connected with electron-motion attenuation it determines half width of the absorption curve. The normalization conditions may be written as follows:

$$\sum_j N_j = N. \tag{3}$$

For free electrons $\omega_j = 0$, and formula (2) describes optical properties of metals. In case of quantum absorption interband transitions expression (2) takes the

* This paper has been presented at the VI Polish-Czechoslovakian Optical Conference in Lubiatów (Poland), September 25-28, 1984.

form

$$\hat{\varepsilon} = 1 + \frac{4\pi e^2}{m} \sum_j \frac{Nf_j}{(\omega_j^2 - \omega^2) - i\gamma_j \omega} \tag{4}$$

where $\hbar\omega_j$ denotes an energy which separates the two states, f_j is a probability of quantum transition between those states, the following normalization condition

$$\sum_j f_j = 1 \tag{5}$$

being satisfied. Expression (4) may be written in the following way:

$$\hat{\varepsilon} = 1 + \sum_j \frac{f_j \omega_p^2}{(\omega^2 - \omega_j^2) - i\gamma_j \omega} \tag{6}$$

where $\omega_p = \sqrt{4\pi Ne^2/m}$ denotes plasmon frequency. Taking account of the types of interactions between the wave and the medium, relations between real and imaginary parts of dielectric permittivity and the optical constants may be given basing on Eq. (1) as follows:

$$\varepsilon_1^{(f)} + \varepsilon_1^{(b)} = \varepsilon_1 = n^2 - k^2, \tag{7}$$

$$\varepsilon_2^{(f)} + \varepsilon_2^{(b)} = \varepsilon_2 = 2nk. \tag{8}$$

Expression (8) attains maximum in a spectral range in which resonance absorption occurs. The plot of ε_2 for the above types of absorption, i.e., the classical one labelled (f), and quantum one labelled (b), is shown in Fig. 1 [5].

Resonance effects determined by the ε_2^b term are connected with the crystal structure and they vanish when the phase transition into liquid state [6] or into amorphic one [7] occurs which is illustrated in Figs. 2 and 3.

Optical properties may be also described with energetic coefficients of reflectivity and transmittivity as well as their wave-frequency dependences. Plasmon frequency devides area of ω into a range in which the medium exhibits

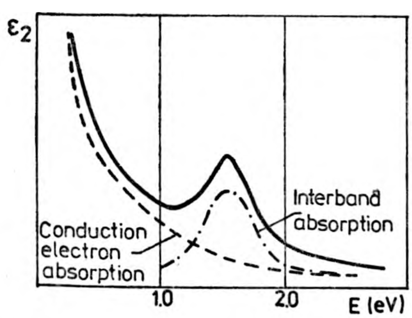


Fig. 1

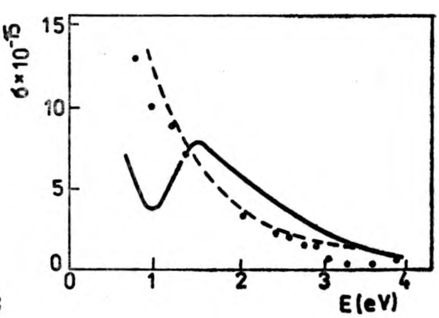
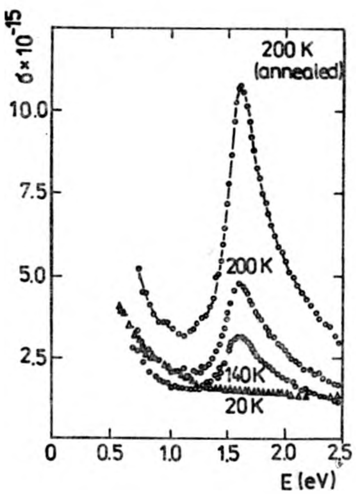


Fig. 2

Fig. 1. Aluminium absorption spectrum [5]

Fig. 2. Comparison of liquid (— — — —) and solid (————) Al [36]

Fig. 3
▼



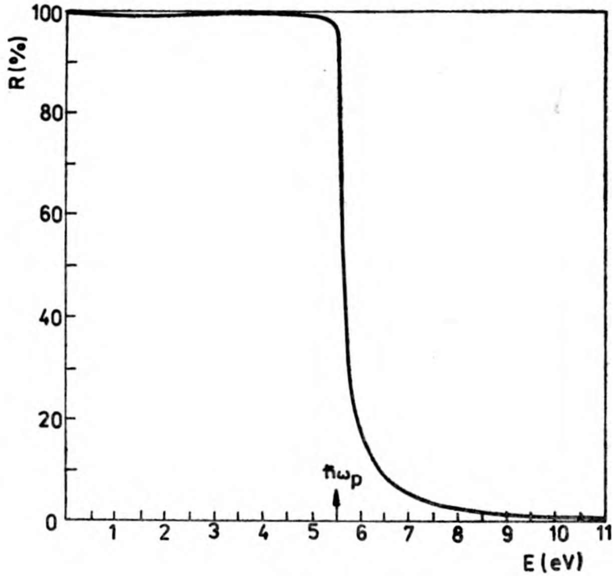


Fig. 3 Influence of the substrate temperature on the absorption spectrum of evaporated Al films [37, 38]

Fig. 4. Spectral dependence of reflectivity for a free-electron metal [2]

Fig. 5
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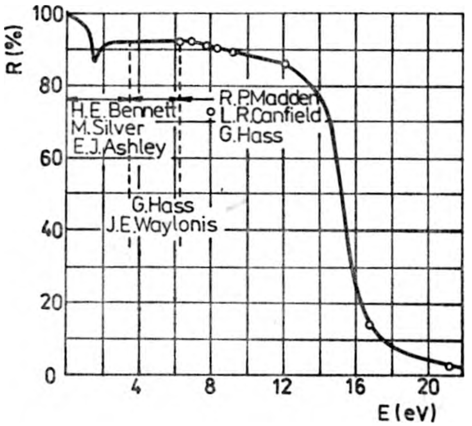

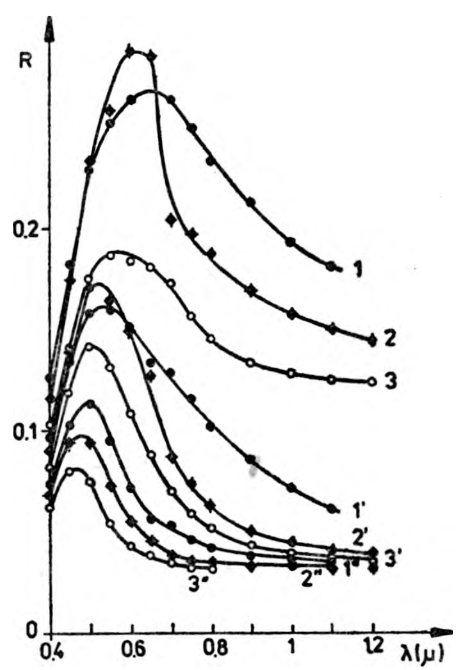

Fig. 5. Reflectance for aluminium. The decrease in reflectance at $\hbar\omega = 1.4$ eV arises from a weak interband transition. The large decrease in reflectance at $\hbar\omega = 14.7$ eV identifies the plasma resonance [8]

Fig. 6. Spectral dependence of reflectivity for Ag films grown with different rates of evaporation [15]

high reflectance for $\omega < \omega_p$ and the one with high transmittance for $\omega > \omega_p$. Theoretical [8] and experimental [9] plots of R vs. $\hbar\omega$ for aluminium are shown in Figs. 4 and 5, where the plasmon frequency is also indicated. Optical properties which can be explained on a basis of Drude-Lorentz- and interband-transition theories are called the normal ones. Theoretical results are in a good agreement with the experimental ones for bulk materials and thick films [10–13].

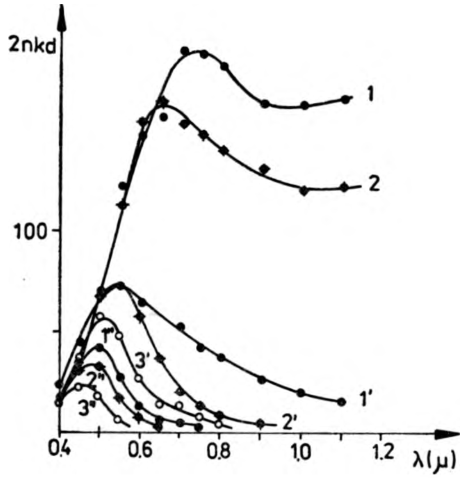

Fig. 8

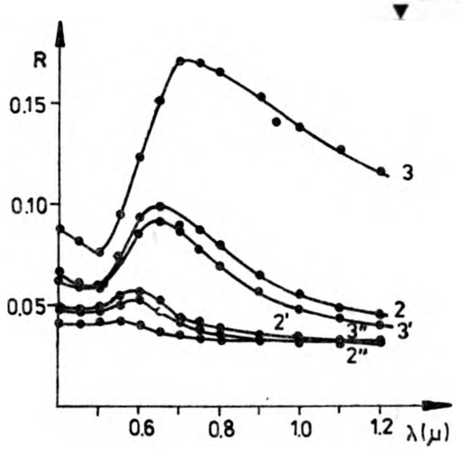

Fig. 7. Imaginary part of dielectric permittivity ε_2' as a function of wavelength λ for Ag films grown with different rates of evaporation [15]

Fig. 8. Spectral dependence of reflectivity for Au films with different thicknesses [15]

Optical investigations of colloidal media, island films and coarse films show existance of phenomena which cannot be explained on grounds of the above theories and these properties are called the anomalous ones.

As structural studies show, the films in their initial stage of growth when evaporated under appropriate conditions exhibit an island structure. Optical properties of the films exhibit anomalies consisting in existance of absorption peaks which are not connected with interband transitions, but which are dependent upon the film microstructure characterized by the volume fraction q defined as

$$q = V_{\text{microparticles}}/V_{\text{film}}. \tag{9}$$

Parameter q can be determined basing on microscopic pictures according to the method presented in paper [14] where

$$q = \frac{2}{3}l, \tag{10}$$

l is a ratio of segments' lengths crossing the islands and the total length. Parameter q may range from 0 which corresponds to the non-evaporated substrate to 1 which corresponds to the continuous film. Resonance effects have been observed in case of metallic island films on amorphic and crystalline substrates [15–21]. For thin films when $d/\lambda < 1$, the imaginary part of the film dielectric permittivity ε_2' may be experimentally determined from the Wolter's approximation [22]

$$\varepsilon_2' = \frac{\lambda}{2\pi d} n_s \frac{1-R-T}{T}, \tag{11}$$

d being the film thickness, λ – wavelength, n_s – refractive index for the substrate R and T – energetic coefficients of reflectivity and transmittivity, respectively determined experimentally. Experimental plots of reflectivity coefficient and

Fig. 9
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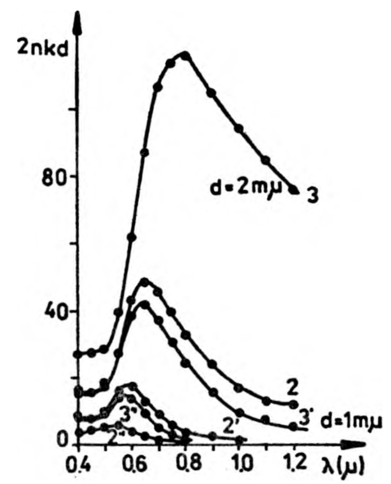

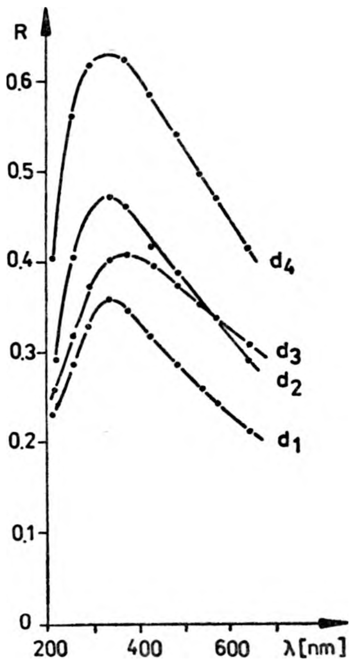

Fig. 9. Imaginary part of the permittivity ε_2' as a function of wavelength λ for Au films with different thicknesses [15]

Fig. 10. Reflectivity spectrum for Al island films with different volume functions [28]

imaginary part of the dielectric permittivity as a function of wavelength are given in Figs. 6–11 for silver-, gold- and aluminium films, respectively. As can be seen from the figures the plots of ε_2' are clearly of the resonance-like character, and the wavelength for which the maximum of ε_2' is observed depends upon the covering degree determined by the volume fraction. With the increasing q, λ_{max} is shifted towards the longer waves. For explanation of these effects some micro-theories have arisen which are concerned with interactions between electromagnetic wave and an isolated system of metallic islands on the dielectric substrate, being the dipole system.

One of the first was the micro-theory of Maxwell-Garnett [23] which dealt with the arrangement of spherical metallic grains on an insulating substrate. The dielectric permittivity of such an arrangement is expressed as follows:

$$\hat{\varepsilon}' = 1 + 4\pi N'_* \mathfrak{a} = 1 + 4\pi \frac{\boldsymbol{P}}{\boldsymbol{E}} \tag{12}$$

where

$$\boldsymbol{P} = N_* \mathfrak{a} \boldsymbol{E}_{\mathrm{L}} \tag{13}$$

is polarization and N_* denotes the island density, $\mathfrak{a}$ – metallic island polarizability and $\boldsymbol{E}_{\mathrm{L}}$ – local field. Next, some completions and modifications such as considering grain shape and their mutual interactions were assumed. David [24] assumed that the islands were elliptical and they did not interact with one another. Furthermore, a structural factor f so-called shape factor, was introduced which was a function of the ellipsoid half-axes ratio (b/a). For the spherical particles $f = 1/3$. The obtained expression [24] for the imaginary part of the

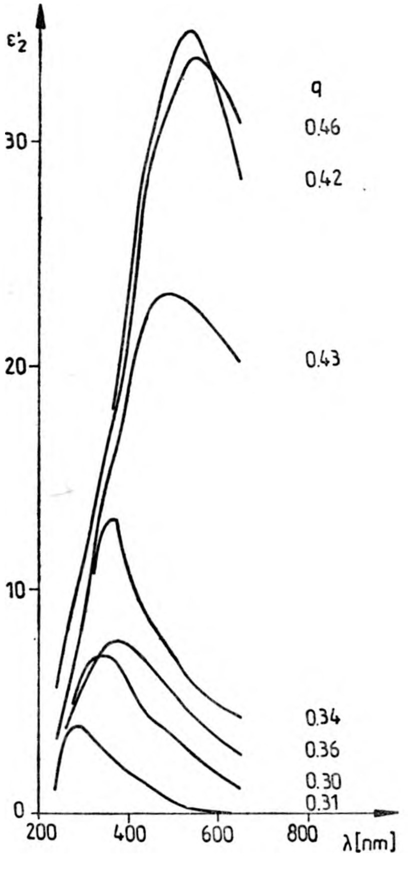

Fig. 11. Imaginary part of the permittivity ε'_2 as a function of wavelength λ for Al films with different volume fractions [28]

permittivity for the film is the following:

$$\varepsilon_2' = \frac{q\varepsilon_s\varepsilon_2}{[\varepsilon_s+(\varepsilon_1-\varepsilon_s)f]^2+f^2\varepsilon_2^2} \tag{14}$$

where ε_1, ε_2 – real and imaginary parts of the metal permittivity, respectively, ε_s – the substrate permittivity.

Doremus [25] assumed the Maxwell-Garnett model of spherical particles which interacted with one another as electric dipoles. The local field $\boldsymbol{E}_L$ may then be expressed as

$$\boldsymbol{E}_L = \boldsymbol{E}_E + \boldsymbol{E}_I \tag{15}$$

where $\boldsymbol{E}_E$ is an external field, and $\boldsymbol{E}_I$ is an internal field determined from the Lorentz-Lorenz formula. The expression for the film-permittivity's imaginary part takes the form

$$\varepsilon_2' = \frac{9qn_s^2\varepsilon_2}{(1-q)^2\left[\varepsilon_1+n_s^2\left(\frac{2+q}{1-q}\right)+\varepsilon_2\right]}. \tag{16}$$

Using the estimated relations of ε_1 and ε_2 with wavelength (λ) [26] Doremus determined the relation between the wavelength λ_{max} for which ε_2' attained maximum and the volume fraction. It is as follows:

$$\lambda_{max} = \lambda_c\sqrt{\varepsilon_0+n_s^2\left(\frac{2+q}{1-q}\right)} \tag{17}$$

where λ_c denotes a characteristic quantity for a given metal.

A further modification was introduced by Jarrett and Ward [27]. Basing on a plentiful experimental material the authors [27] assumed the island film model as an arrangement of ellipsoidal grains which interacted in a dipole-like way. In this case the film-permittivity's imaginary part is expressed in the following way:

$$\varepsilon_2' = \frac{q\varepsilon_s\varepsilon_2}{[\varepsilon_s+(\varepsilon_1-\varepsilon_s)F]^2+\varepsilon_2^2F^2} \tag{18}$$

where F is a structural factor dependent upon the grain shape and the volume fraction. In this model F is expressed as follows:

$$F = f-\frac{1}{3}q. \tag{19}$$

When neglecting the interactions between islands ($F = f$), then the result of David [24] is obtained (Eq. (14)). When assuming the spherical island model

$f = 1/3$ where the islands interact in a dipole-like way, then

$$F = \frac{1}{3}(1-q) \tag{20}$$

and Doremus' expression [25] is obtained (Eq. (16)).

In order to compare the experimental course of ε_2' determined from Eq. (11) with the theoretical one calculated from Eq. (18) the parameter F should be determined. This can be done by two independent methods. The first one consists in determination of ε_2'/q vs. λ from Eq. (18) for given values of F. The curves possess maxima for certain wavelengths. Next, the relation of F as a function of the wavelength $\lambda_{\max}$ for which the maximum has occurred in $\varepsilon_2' q$ vs. λ should

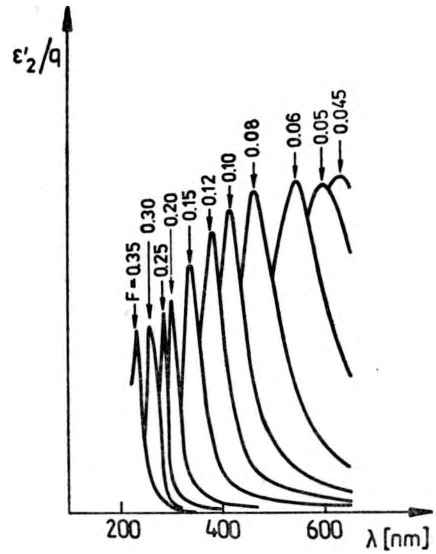

Fig. 13

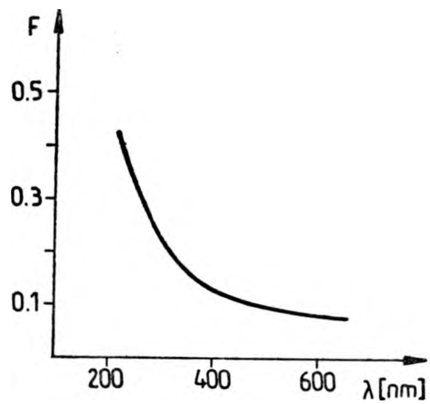

Fig. 12. Calculated value of ε_2'/q for Al films as a function of wavelength λ for different values of F

Fig. 13. Variation of F as a function of wavelength $\lambda_{\max}$ corresponding to maximum absorption peak for Al films

be given. The examplary plots of the above relations are presented in the respective Figs. 12, 13 for aluminium films. Basing on the experimental curve of ε_2' vs. λ the wavelength corresponding to the maximum of ε_2' is determined, and next, on a basis of Fig. 13 the parameter F is specified.

The other method consists in substituting the experimental value of ε_2' corresponding to the absorption maximum into Eq. (18). In Figures 14 a, b, c, the theoretical and experimental curves for aluminium island films are plotted for the volume fractions of $q_1 = 0.31$, $q_2 = 0.34$, $q_3 = 0.43$, respectively. As can be seen the theoretical and experimental curves agree for $0.3 \leqslant q \leqslant 0.43$ in the way that their maxima coincide with each other. When $q = 0.45$ the observed effects cannot be described with the presented model. With the increasing q the island diameters increase, and the island shape becomes more and more irregular. In this case an assumption about ellipsoidal shapes of the islands ceases to be valid. Moreover, with the increasing q the film approaches the percolation threshold, which limits the application of the island-film model to a description of the anomalous optical absorption [28].

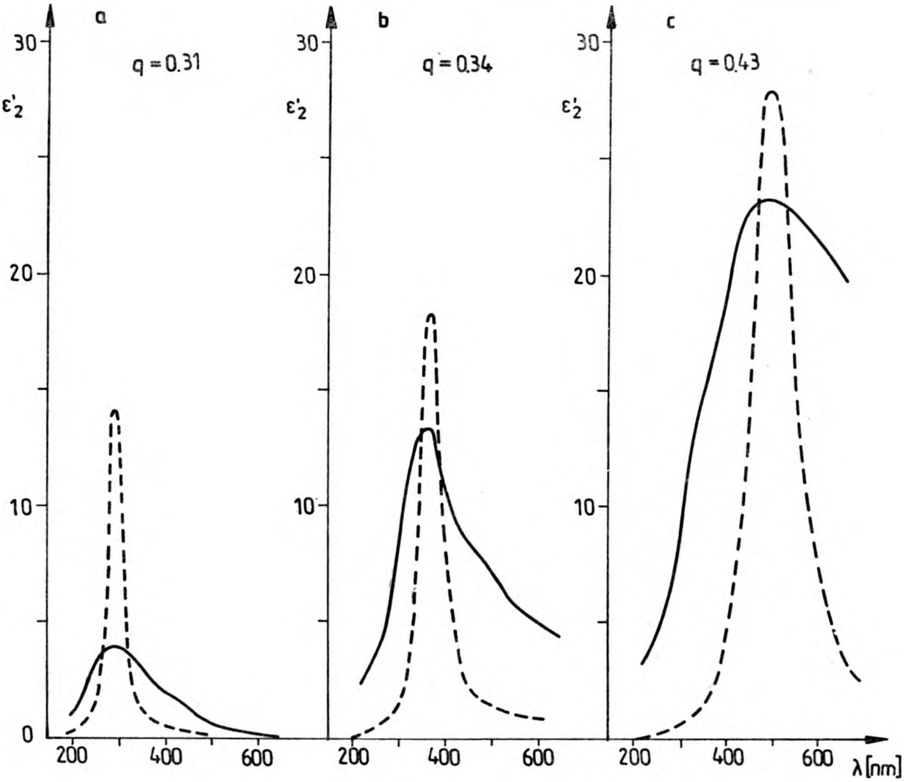

Fig. 14. Experimental (————) and theoretical (— — — —) curves of ε_2' for Al films: a) $q = 0.31$, b) $q = 0.34$, c) $q = 0.43$

For the island films, distinct absorption maxima are observed which are shifted towards longer waves with the increasing q. From Eq. (18) and from relations between ε_1, ε_2 and λ the dependence of $\lambda_{\max}$ upon F can be determined as

$$\lambda_{\max} = \lambda_0 \sqrt{\varepsilon_0 + \varepsilon_s\left(\frac{1}{F} - 1\right)}. \tag{21}$$

Basing on Eqs. (17) and (21) the dependences of $\lambda^2_{\max}$ upon $2+q/1-q$ and $1/F-1$, respectively, have been plotted in Figs. 15 and 16. It can be concluded that expression (21) describes the dependence of $\lambda^2_{\max}(F)$ better than formula (17) [28].

An attempt of another explanation of optical properties of island films was undertaken by Hampe [29] who assumed that in an isolated island, free elec-

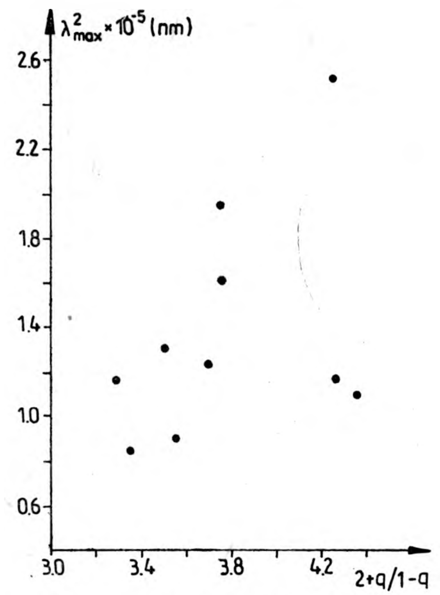

Fig. 15. Plot of $\lambda^2_{\max}$ against $2+q/1-q$

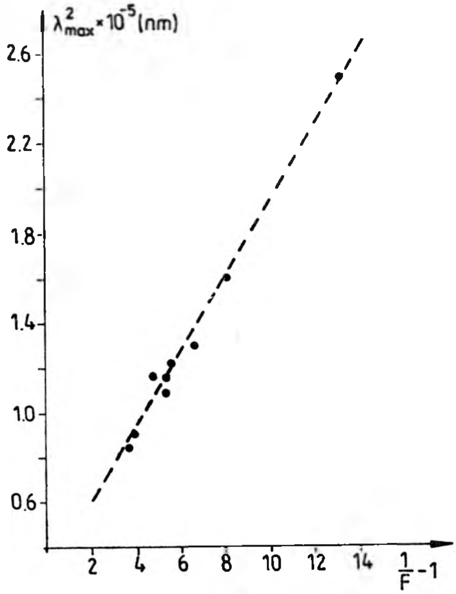

Fig. 16. Plot of $\lambda^2_{\max}$ against $1/F-1$

trons due to electromagnetic wave were subject to plasmon oscillations described with the equation

$$\ddot{\boldsymbol{r}}+\gamma\dot{\boldsymbol{r}}+\omega_{0s}\boldsymbol{r} = \frac{e}{m}\boldsymbol{E}_{\mathrm{L}} \tag{22}$$

where $\omega_{0s} = \omega_{\mathrm{p}}/\sqrt{3\varepsilon_*}$ is the free-oscillation frequency of electrons in the islands, ε_* denotes dielectric permittivity of a medium in which the island is situated. For a coarse surface of the substrate the permittivity equals [30]

$$\varepsilon_* = \frac{n_0^2+n_{\mathrm{s}}^2}{2} \tag{23}$$

where n_0, n_{s} are refractive indices for the air and substrate, respectively. The internal field $\boldsymbol{E}_{\mathrm{I}}$ connected with dipole interaction was determined from the Lorentz-Lorenz formula similarly as in paper [27]. Basing on this theory an attempt of description of optical properties of Au-on-SiO_2- [31] and Ag- [32] island films was undertaken, however, some discrepancies between theoretical and experimental results occurred and it was particularly true for the plasmon frequencies. Therefore, SHKLYAREVSKII [33] modified the Hampe model and assumed that spherical dipoles were in the medium of the permittivity determined by

$$\tilde{\varepsilon} = q\varepsilon_{1\mathrm{b}}+(1-q)\,\varepsilon_0 \tag{24}$$

where ε_{1b} – real part of the metal's permittivity connected with quantum absorption (Eq. (7)). The internal field $\boldsymbol{E}'_{\mathrm{I}}$ was determined by summation of interactions coming from the remaining dipoles islands

$$\boldsymbol{E}'_{\mathrm{I}} = \boldsymbol{E}_{\mathrm{I}}\sqrt{q} \tag{25}$$

where $\boldsymbol{E}_{\mathrm{I}}$ specified an internal field from the Lorentz-Lorenz formula, and polarization equaled

$$\boldsymbol{P} = qNe\boldsymbol{r} \tag{26}$$

where $\boldsymbol{r}$ was a solution of Eq. (22). Under the above assumptions the permittivity's imaginary part expresses itself as

$$\varepsilon'_2 = \frac{q\omega_{\mathrm{p}}^2\gamma\omega}{(\omega_{0\mathrm{q}}^2-\omega^2)^2+\gamma^2\omega^2} \tag{27}$$

where $\omega_{0\mathrm{q}}$ denotes free-oscillation frequency.

For a frequency approximately equal to the resonance frequency ($\omega \approx \omega_{0\mathrm{q}}$) Eq. (27) takes the form

$$\varepsilon'_2 = \frac{q\omega_{\mathrm{p}}^2}{\gamma\omega_{0\mathrm{q}}}. \tag{28}$$

By using the experimentally determined value of ε'_2 for the resonance frequency the half width γ can be determined from Eq. (28), and next, on a basis of formula (27) the theoretical dependence of ε'_2 upon ω can be calculated. Theoretical and

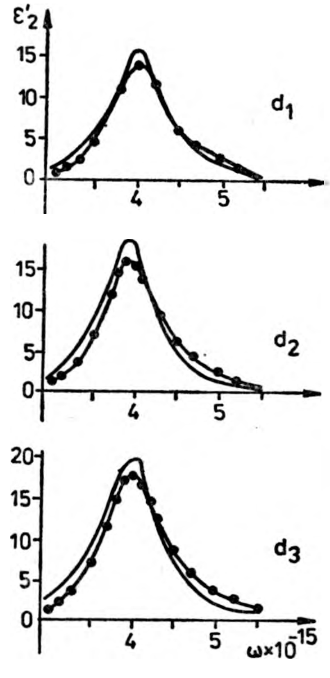

Fig. 17. Experimental (—•—•—•—) and theoretical (———) curves of ε'_2 for Ag films with different thicknesses [33]

experimental dependences of ε_2' for silver films of various thicknesses, i.e., various volume fractions are presented in Fig. 17. As can be seen from the figure the agreement is good [33].

For explanation of the island film properties calculations of ε_2' vs. λ according to Eqs. (27) and (28) have been performed for aluminium films of various volume fractions in order to compare applicabilities of the Maxwell-Garnett- and Hampe-Shklyarevskii theories to these films. The results are presented in Fig. 18 along

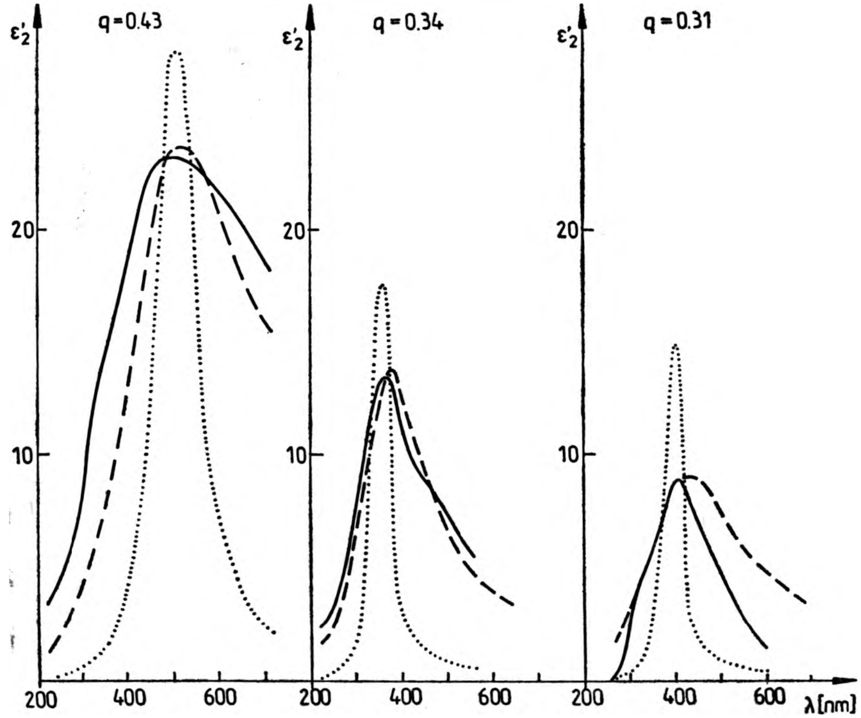

Fig. 18. Experimental (————) and theoretical (. . . . . .) Maxwell-Garnett- and (— — — —) Hampe–Shklyarevskii theories curves of ε_2' for Al films with different volume fractions

with the experimental and theoretical curves obtained from the modified Maxwell-Garnett theory Eq. (18). It is easily seen that the Hampe-Shklyarevskii theory yields a better agreement with the experimental data In the subsequent papers the free-oscillation frequency, ω_{0q}, entering Eq. (27), was determined more accurately by taking account of the attenuation characterized by the coefficient γ [34].

In the last decades a relatively large number of papers have been published in the worldwide literature which have been concerned with physical properties of island films attracting great attention for their practical applications, i.a., in cermets, microelectronic and optic elements, etc. Electric and optic properties of the island films, dependent upon their microstructure, differ essentially from those of the continuous films. Change in the microstructure renders modification of physical properties possible. Due to the different conduction mechanisms, the resistivities of the island films exceed those of the continuous films by about six orders of magnitude, and furthermore, the temperature coefficient of resistance in case of the former is negative. Optical properties of the island films, as has been shown above, exhibit anomalies, the correlation between electric and optic properties being found. When approaching to the percolation threshold $q \approx 0.47$ the film resistance drastically decreases until it attains the value for the continuous film. Simultaneously the temperature coefficient of resistance becomes positive [35] and optical anomalies vanish entirely.

Acknowledgement – I wish to thank Dr. A. Radosz for numerous discussions and Mr. P. Biegański for performing the calculations.

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Received November 29, 1984

Оптические аномалии в островных слоях металлов

Обсуждены оптические свойства островных слоев металлов. Дан обзор экспериментальных результатов, иллюстрирующий оптические аномалии Ag, Au, Al. Представлены модифицированные теории Максвелла–Гарриетта, а также Гампе–Шкляревского, которые применяются для объяснения оптических свойств островных слоев. Чтобы сравнить выщеуказанные теории, их применили для островных слоев алюминия.