OPTICAL PROPERTIES AND STRUCTURE OF THIN GOLD FILMS

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Summary

Reflectivity and transmission of goldfilms of known thickness were measured as a function of wavelength. The quantities n and k were determined from these experiments. For a thickness below 10 mμ n and k vary due to the decrease of the mean free path of the free electrons. The light-absorption of the thinnest films is explained with the help of the hypothesis, that they consist of gold in amorphous state. Some ultra-microscopic observations show that the colours of thin films can not be explained on the base of the idea of a colloïdal structure of the films.

Some results of recristallisation are discussed.

The electrical and optical properties of very thin metal layers show an anomalous behaviour. Several explications have been proposed for this facts, the two most important ones are the following.

The mean free path of the electrons is lower than in the bulk metal by collisions with the film boundaries [1]. An other explanation is given taking into account the hypothesis of a colloïdal structure of the film [2].

For the case of gold R e i n d e r s and H a m b u r g e r concluded from their ultra-microscopical observations, that the colour of very thin gold films — which can be red, violet and blue — is due to a colloïdal structure, which is analogous to the colour of the goldsol.

It seems to be interesting to investigate the phenomena in a more quantitative way.

We have measured therefore the reflectivity and transmission of gold films of known thickness. Further we have performed ultra-microscopical observations for the same films and studied the influence of temperature on the structure.

The goldfilms were obtained by evaporation of pure gold in high vacuum ($< 10^{-6}$ mm) from a tungsten spiral on glass plates. The glass plates — thick 0,75 mm, diameter 40 mm — were all cut out of

one plate of high polished glass. They were cleaned by first treating them with hot chromic acid and then with nitric acid for several days. Before being used the clean plates were rinsed with water, then with alcohol and finally rubbed very carefully with fine blotting paper.

The quantity of the metal evaporated on the plates was determined with the aid of a microbalance, by weighing the plates before and after the evaporation. The accuracy of the microbalance was 2γ, so the error in the value of the quantity of metal per cm^2 was less than $\frac{1}{2}\gamma/cm^2$.

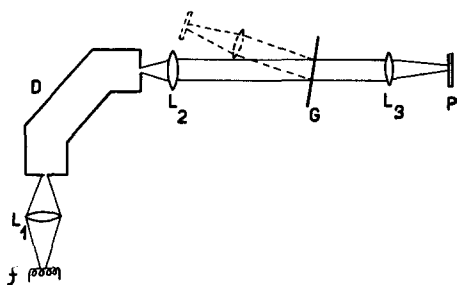Fig. 1 shows the arrangement used for the measurement of reflectivity and transmission.

Fig. 1.

A parallel beam of monochromatic light falls on the goldfilm G under an angle of $7°$ with the normal. The beam is obtained from a filament lamp, connected to constant voltage so that the current is constant to about $1°/_{00}$, combined with a double monochromator. The lense L_3 focusses the light on the rectifiercell P, connected with a M o l l galvanometer. In order to measure the reflection on the boundary gold-air, the rectifiercell and lense L_3 could be turned in the dotted position. The deflection of the galvanometer was photographically registrated on the drum of a registering box. The middle slit of the double monochromator moved synchronically with the drum. In this way we could obtain the transmission and the reflectivity as an continuous function of wavelength in the range from 4500 till 9000 Å. The calibration of wavelength was obtained by giving a current pulse to the galvanometer at known positions of the middle slit.

In fig. 2 and 3 the reflectivity I_R resp. the transmission I_D are plotted as a function of the quantity of metal per cm^2 at several wavelengths. We have assumed that we can use the value of the density of the bulk metal for our layers. These figures also show the reflectivity and the transmission in their dependence of the thickness of the layer.

By means of the method indicated by V e e n e m a n s [3]) and the somewhat quicker one developed by M u r m a n n [4]) the optical

constants n and k can be determined from the data obtained. M u r-
m a n n   has calculated the functions:

$$I_D\,(n,\,k,\,d,\,\lambda)\ \text{and}\ I_R\,(n,\,k,\,d,\,\lambda)$$

Using his expressions we get from the measured values of I_D and
I_R at given wavelength
for each fixed value of
d/λ a curve in the n-k-
plane. The intersection
of these curves gives the
values of n and k. Some-
times the intersection-
point was rather un-
certain. To avoid the
error caused by this un-
certainty, we have de-
termined from n and k
the relation between I
and d and have chosen
such values of n and k
that they fitted in the
best way the experi-
mental curve for I_R and for I_D at the same time.

Fig. 2.

Our procedure shows at the same time for what range n and k
are independent of the thickness of the layer. In fig. 4 the values of n
and k are represented as a function of the wavelength. The values
derived from this figure are indicated in table I.

TABLE I

λ	5000	5500	6000	6500	7000	7500	8000	8300
n	1,10	0,68	0,51⁵	0,43	0,37	0,32⁵	0,28	0,26
k	2,02	2,72	3,31	3,87	4,45	5,01	5,56	5,92

We point to the remarkable fact shown by fig. 2, i.e. a sudden in-
crease in reflectivity at a thickness of about 10 $m\mu$. Values for n and
k which are independent of thickness of the layer cannot explain the
increase mentioned. P o g a n y [5) — who used the polarisation-
method, due to F ö r s t e r l i n g — has found the same fact. In
his experiments the quantity $2nk$ shows an increase at the same thick-
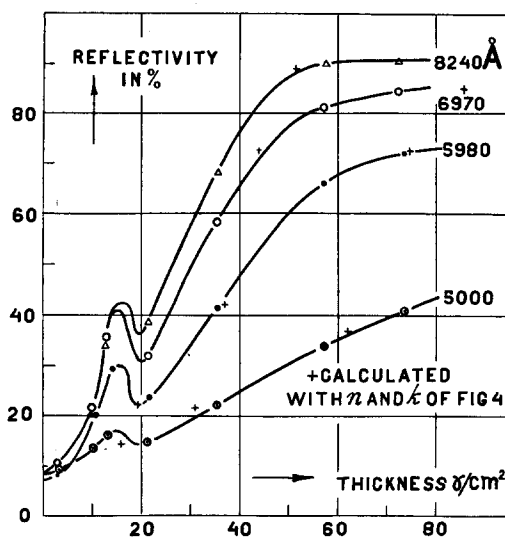ness, reaches a maximum at 2 $m\mu$, and decreases for still smaller

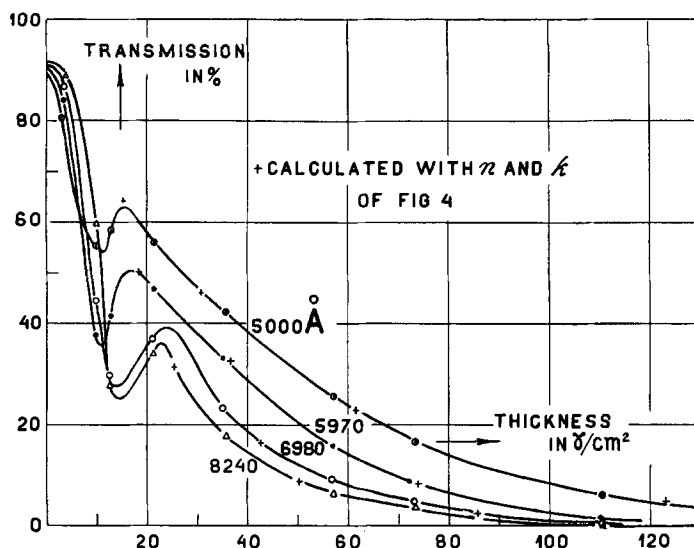values of the thickness. Our measurements don't admit the determination of n and k in this range.
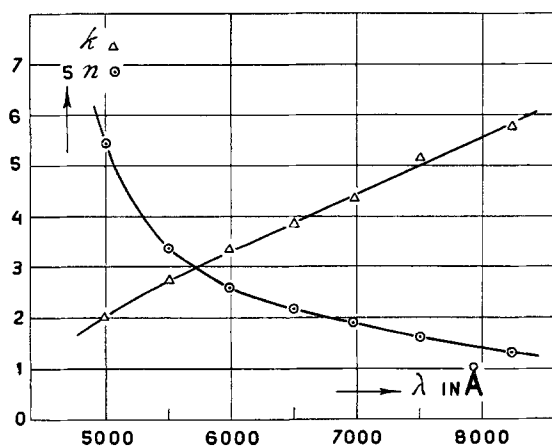

Fig. 3.

Fig. 4.

This range in which the optical constants show the anomalous behaviour is exactly that in which the blue and red coloured films occur, which show particles when examined ultramicroscopically.

Fig. 2 shows that the reflectivity strongly increases with the wavelength in the case of green layers. For red and blue layers this

quantity on the contrary is hardly dependent of wavelength. Their colour is caused by the extinction of the light. We have plotted in fig. 5 for some of our layers the value of the quantity of A defined by

$$\frac{100-R-D}{100-R} \cdot 100,$$

which measures the quantity of light lost by absorption and scattering together. For the case of green films the value of A is independent of the wavelength above about 5000 Å. The thin layers show a remarkable maximum of absorption, which shifts to shorter wavelength with decreasing thickness. The intensity of the scattered light is so weak, that we can neglect it compared with the value of A; so that value is due to the absorption.
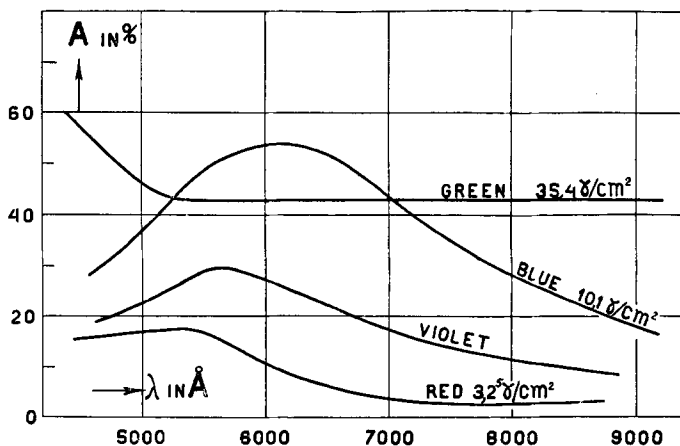

Fig. 5.

In order to explain the colour of thin gold films the hypothesis has been proposed, that they can be compared with colloïds. We have tried to control this hypothesis by some ultramicroscopical observations. We used a Z e i s s microscope with a paraboloïd condensor. The magnification amounted about 700 times. It was necessary to change the method of cleaning in order to obtain glass plates that showed a dark field in the ultramicroscope. First the plates were rinsed with alcohol, then rubbed with fine blotting paper and finally washed in carbontetrachlorid.

The mean results can be summarised as follows.

1°. Blue layers show a mosaic structure, the mean distance between the particles is about $2\,\mu$ — the same is true for thicker layers.

2°. Red and very thin blue layers show a complete dark field.

3°. The number of particles in the ultramicroscopic image for the case of 1°. is independent of the thickness of the layer.

4°. The colour shown by the particles themselves is nearly the same for all layers, viz. orange yellow; the intensity of the images varies, however, with the thickness. Yet this intensity of the particles is so small, that the value of A cannot be explained by their scattering of the light.

5°. In the range of thickness between 1°. and 2°. two specimen evaporated together are such that one shows particles and the other not, although the blue colour of both was the same.

From these facts it seems improbable that the colours of the films are caused by a colloïdal structure of the layers. A still stronger argument against this conception lies in the fact that below a thickness of 10 mµ the sudden increase of the reflection occurs.

A film, which consists of separated particles, never can possess a greater reflectivity than a thicker homogeneous one.

The supposition occurs probable that the layers consist of a homogeneous layer in which particles are cubed in.

We now have to discuss the important fact, that the absorption coefficient k of the homogeneous layer rises at a given thickness. One should be inclined to give for this fact with L o v e l l (loc. cit.) the explanation, that the mean free path below a certain critical thickness is a function of this quantity — the quantitative agreement shown in his works seems promising. When the formula of L o v e l l is applied to the optical theory of metal, one get an increase of the reflectivity below a thickness of 10 mµ in agreement with our experiments. It is, however, impossible to give a quantitative description of the experimental result of P o g a n y [6]) who determined the maximum of k at a thickness of 2 mµ, the theory giving a maximum at 0,2 mµ *).

*) According to the theory, the mean free path at roomtemperature is given by

$$\lambda_\theta = \frac{Ne^2}{2mv} \cdot \frac{1}{\rho_\theta} = 68,5 \text{ mµ.}$$

L o v e l l deduced that for a thickness small against the value of λ_θ, the new mean free path is

$$\lambda' = d\left(1 + \ln \frac{\lambda_\theta}{d}\right).$$

The influence of a variation of λ' upon the optical constants can be calculated with the aid of the dispersion theory of metal:

$$n^2 - k^2 = 1 - \left(\frac{\lambda}{\lambda_0}\right)^2 \cdot \frac{1}{1 + (\lambda/\lambda_\tau)^2} + \chi_1;$$

Though the shortening of the mean free path of the electrons indeed will cause the variation of the optical constants in the layers of a thickness about 7 mμ, in very thin layers another effect seems to occur. In our opinion it must be supposed, that in these layers the metal is in an amorphous state, bound to the glass surface by adsorption.

S u h r m a n n and B a r t h [7]) have proved that at low temperatures the metal occurs in this state and that it at higher temperature changes into the normal metal. The stability of amorphous metal became greater at decreasing thickness.

The following facts support our hypothesis:

1°. with decreasing thickness of the film the maximum of the absorption shifts to shorter wavelengths (see fig. 5); with decreasing number of free electrons the red absorption will yet diminish.

2°. A red film shows an instability; in the course of some days it turns blue. The maximum of absorption shifts from 5400 Å till 6000 Å.

3°. A red film, deposited at —180°C, becomes blue after raising the temperature till 20°C. Apparently thick amorphous red layers are only stable at low temperatures.

Finally some phenomena observed by heating of the same gold-films may be mentioned:

1°. A blue film turns red by heating it at 150—250°C. By means of microweighing it appears, that the amount of metal was the same before and after heating.

2°. When such a red film is breathened, it changes into a blue one again. However, this blue colour is quite different from the original one. The absorption has diminished; the layer has changed.

$$2nk = \left(\frac{\lambda}{\lambda_\cdot}\right)^2 \cdot \frac{\lambda}{\lambda_T} \cdot \frac{1}{1 + (\lambda/\lambda_T)^2} + \chi_2$$

in which $\lambda_0^2 = \pi e^2\, m/Ne^2$ and $\lambda_T = 2\pi\, mc\, \sigma_0/Ne^2$; χ_1 and χ_2 is that part due to the inner photo-electrical absorption. From the values of the constants of gold and from those of n and k (table I) we have determined χ_1 and χ_2. With the aid of L o v e l l's formula we know the decrease of the electrical conductivity σ_0 and so of λ_T as a function of the thickness. Supposing χ_1 and χ_2 independent of thickness we get an increase of $2nk$ below 10 mμ, with a maximum at 0,2 mμ. The value of $n^2 - k^2$ yet remains constant till 0,5 mμ.

P o g a n y made an analogical calculation, using the classical dispersion theory and the supposition of W. P l a n c k

$$\lambda' = \frac{\lambda\theta}{1 + \alpha/d} \cdot$$

He chose the value of α thus, that the maximum of $2nk$ occurs at the thickness of 2 mμ.

3°. It appears from ultramicroscopical observation, that this red film shows particles; the mean distance is the same as before heating. The colour of the scattered light is of a brighter yellow as before heating, and the intensity of the scattered light has increased. Breathening causes open spaces in the field and at the other side on certain spots the ultramicrons are accumulated. The colour of the particles changed towards the red.

The facts mentioned make it probable that a recrystallisation has taken place. The particles grow at the cost of the material of the homogeneous underlayer, their number remains the same. In this case the colour probably is caused by a colloïdal structure of the layers.

Summarising we may describe the process of evaporation of gold on glass in the following way: At first the gold is adsorbed by the glass in an amorphous state, at increasing thickness the layer changes more and more into the crystallinic state, and the observed optical phenomena can be explained with the help of the dispersion theory of metals.

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