JULY 1, 1931 PHYSICAL REVIEW VOLUME 38

INTERFERENCE IN THIN METALLIC FILMS

By Hiram W. Edwards
University of California at Los Angeles

(Received February 2, 1931)

Abstract

The phenomenon of the colored appearance of thin metallic films sputtered upon glass or upon other metals, when viewed in white light, is explained as being caused by interference. Some qualitative observations of cyclic changes of color are given which support this viewpoint. Mathematical expressions are derived from Maxwell's electromagnetic equations to express the change of phase as the wave train is reflected from a metal surface in air, from metal in metal, for refraction as the wave enters the metal from air and from air into metal.Use of the values of the indices of refraction and absorption for massive metals indicates fair substantiation of experimental results. Fritze's values of the optical constants for thin metals do not seem to give agreement between theory and experiment. The thickness of the film of copper necessary to produce a yellow color (interference for $\lambda = 0.48\mu$) when calculated from the index of refraction (1.13) is found to be three and one-half times larger than the value found by weighing the total deposit. The balance of evidence seems to support the theory of interference.

Introduction

AN OCCASIONAL observation has been made of the fact that thin metallic films may appear to be variously colored when viewed in normal white light. Fritze[1] noticed that the color of a film of silver sputtered upon glass first appeared blue, then changed to violet and finally a clear red as the thickness increased. When red, the film thickness was from 2.4 to $2.9\mu\mu$. A chemically deposited silver film had likewise a red color when $4.7\mu\mu$ thick. Fritze offers no explanation other than that the color is a characteristic of pure silver in a film of such a thickness.

Other observers have thought that the color observed was due to some chemical compound. Recently Bockstahler and Overbeck[2] described "concentric rings of color similar in appearance to Newton's rings," when sputtering tin upon glass. They report a cyclic change of color as the thickness of the film increases. No explanation is offered.

The writer of this article reported[3] the color of nickel films sputtered upon platinum. The thinnest film to show a color appeared to be yellow. With increasing thickness the color changed to orange, purple, blue and then white.

The occasion for this paper is to offer an explanation for the observed phenomenon. It is thought that the production of colors under the indicated circumstances is due to interference between two beams of light in a manner which is very similar to that of the more familiar case of thin soap films or

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[1] Fritze, Ann. d. Physik **47**, 763 (1915).

[2] Bockstahler and Overbeck, Bull. Phys. Rev. **5**, No. 7, Paper 39 (1930).

[3] Edwards, Phys. Rev. **33**, 463 (1929).

oil upon water. The distinguishing feature of the metallic case seems to be the more complicated manner in which difference of phase is produced.

The argument in favor of interference is based upon the following facts all of which have been observed by the writer and some of which have been reported by others:

(1). Colors are produced only when the film is transparent, obviously excluding those colors which are characteristic of massive metals such as the red of copper.

(2). The colors are more intense when a white metal such as silver, nickel, platinum, etc. (and therefore having a high reflection coefficient) lies under a thin film of some other metal.

(3). Several cycles of color may occur as the thickness of the thin film increases. In one case, i.e., that of copper upon silver, five distinct color cycles have been noticed. In this particular, the order was, first yellow then followed by gold, purple, blue and back to yellow. This indicated sequence of colors was also observed with copper upon nickel, and copper upon aluminum.

(4). The intensity of any one color increases up to a maximum in the series of cycles and then decreases. A single case will illustrate. The second appearance of blue when depositing copper upon "tin" foil was the most intense. In this particular case only three cycles were observed. At the first appearance of the blue the film was so thin that the reflecting power of the copper must have been small in comparison with that of the tin foil underneath. In the third appearance the transmission coefficient of the copper must have materially reduced the intensity of the transmitted beam.

(5). The color of the film varies with the angle of incidence which the white light makes with the film. This phenomenon required a change of incidence of 70°–80° in order for the color to make a pronounced change.

(6). In general the same cycle of colors is found to occur even though the pairs of metals used may be different. This is true so far as the writer's observations are concerned. A study of the theoretical considerations indicated that one should not expect the first color to appear to be the same in all cases.

(7). Different thicknesses of a particular metal sputtered upon other dissimilar metals are required to produce the first appearance of a particular color. This phenomenon was observed when sputtering copper upon contiguous strips of silver, nickel, and aluminum.

When considered collectively these facts seem to uphold the explanation of the color production as being one of interference. In addition to this qualitative evidence, a partial corroboration is to be found quantitatively. Equations are derived below which express the difference in phase of the two wave trains concerned in terms of the optical constants of the metals.

Theoretical Treatment

If we may assume that the color phenomenon under consideration is one of interference then we must determine the total difference in phase between the wave reflected from the surface of the metal in contact with air and the wave emerging from that surface after reflection from the surface between the two metals. The total change in phase is due to five factors: (1) reflection at the surface between air and the first metal; (2) refraction at the same surface; (3) reflection at the surface between the two metals; (4) refraction as the ray which passes both ways through the first metal emerges into the air and (5) the optical length of the path traversed by the refracted ray.

In order to find expressions for the change of phase we may start with Maxwell's equation for the propagation of a wave in an absorbing medium

$$\frac{m\epsilon}{c^2}\left(\frac{\partial^2 E}{\partial t^2} + \sigma\frac{\partial E}{\partial t}\right) = \nabla^2 E \tag{1}$$

where m is the magnetic permeability, ϵ the dielectric constant, σ the specific conductivity of the medium, and E the electric field intensity. For the media under consideration we may put both m and ϵ equal to unity. If the wave front is plane and parallel to the Z axis then the equation becomes:

$$\frac{1}{c^2}\left(\frac{\partial^2 E}{\partial t^2} + \sigma\frac{\partial E}{\partial t}\right) = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2}\cdot \tag{2}$$

Since the disturbance is periodic and may be put proportional to $pe^{-i\omega t}$ when p may be complex, we may write

$$-\frac{1}{c^2}(i\omega\sigma + \omega^2)E = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2}$$

or

$$\frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial y^2} + A^2 E = 0 \tag{3}$$

in which A depends upon the constants. A is real only when $\sigma = 0$.

For a particular solution of (3) we have

$$E = E_0 e^{i(ax+by-\omega t)}. \tag{4}$$

Substituting this value of E in Eq. (3) gives:

$$a^2 + b^2 = A^2.$$

If there is no absorption a and b are both real. In the case of absorbing media a and b are both complex and may be expressed as follows

$$a = \frac{2\pi}{\lambda'}\cos\theta + ik_1 \quad b = \frac{2\pi}{\lambda'}\sin\theta + ik_2.$$

If we take the direction of propagation of the wave along x and use the following defining equations

$$k_1 = \frac{2\pi}{\lambda}\kappa\cos\alpha, \quad k_2 = \frac{2\pi}{\lambda}\kappa\sin\alpha, \quad \nu = \frac{\lambda}{\lambda'} = \frac{c}{v}$$

when λ is the wave-length in air and λ' the wave-length in the absorbing medium, then the equation for E becomes:

$$E = E_0 e^{-2\pi\kappa x/\lambda} \cos \frac{2\pi\nu}{\lambda}(x - vt)$$

and

$$a^2 + b^2 = \frac{4\pi^2}{\lambda^2}[\nu^2 - \kappa^2 + 2i\nu\kappa \cos (\theta - \alpha)] \tag{5}$$

$$= \frac{4\pi^2}{\lambda^2}(\nu + i\kappa)^2 \tag{6}$$

if the light is incident normally to the surface. In these expressions ν is the ordinary optical index of refraction and κ the absorption index.

In order to simplify the mathematical detail we shall determine the change of phase for the phenomenon of reflection at the boundary surface between any two media and for refraction as the ray passes from one medium into the other. We shall use the subscript 1 to designate the constants of the first medium and the subscript 2 for the second medium and assume that the wave is plane polarized with E perpendicular to the plane of incidence. We may then write expressions for E as follows:

In the incident wave $e^{i(a_1x+by-\omega t)}$
In the reflected wave $re^{i(-a_1x+by-\omega t)}$
In the refracted wave $se^{i(a_2x+by-\omega t)}$

By the use of the usual boundary conditions, it follows that

$$1 + r = s \text{ and } a_1(1 - r) = a_2 s$$

hence

$$r = \frac{a_1 - a_2}{a_1 + a_2} \quad \text{and} \quad s = \frac{2a_1}{a_1 + a_2}\cdot \tag{7}$$

It may be shown that the wave velocities in the first medium and in the second medium, respectively, are:

$$v_1 = \frac{c}{(a_1^2 + b^2)^{1/2}} \quad v_2 = \frac{c}{(a_2^2 + b^2)^{1/2}}\cdot$$

The ratio of the velocities (v_1/v_2) in the two absorbing media may be defined as the complex index of refraction which we will designate by μ. Hence, using Eq. (6), we may write:

$$\mu = \frac{(a_2^2 + b^2)^{1/2}}{(a_1^2 + b^2)^{1/2}} = \frac{\nu_2 + i\kappa_2}{\nu_1 + i\kappa_1}\cdot \tag{8}$$

In order to simplify this expression we may put $\mu = C + iD$ where

$$C = \frac{\nu_1\nu_2 + \kappa_1\kappa_2}{\nu_1^2 + \kappa_1^2} \quad D = \frac{\nu_1\kappa_2 - \nu_2\kappa_1}{\nu_1^2 + \kappa_1^2}\cdot \tag{9}$$

By assigning the direction of propagation of the disturbance parallel to the x axis it follows that $\mu = a_1/a_2$ and hence Eqs. (7) become:

$$r = \frac{\mu - 1}{\mu + 1} \qquad s = \frac{2\mu}{\mu + 1} \cdot \tag{10}$$

Since r is the amplitude of the reflected wave, assuming the amplitude of the incident wave is unity, the intensity J^2 and change of phase δ may be found in the usual manner by putting

$$r = Je^{i\delta} = \frac{C - 1 + iD}{C + 1 + iD} \cdot$$

If the right hand member is designated by the symbol M and N is used for the conjugate of M, then the intensity of the reflected wave is

$$J^2 = MN = \frac{(C - 1)^2 + D^2}{(C + 1)^2 + D^2} \tag{11}$$

and the desired expression for the change in phase of the reflected wave is:

$$\tan \delta = \frac{M - N}{i(M + N)} = \frac{2D}{C^2 + D^2 - 1} \cdot \tag{12}$$

The change in phase which the wave experiences on refraction is found in a similar manner using the expression for s, as given in Eq. (7), as a starting point. The result is

$$\tan \delta = \frac{D}{C^2 + D^2 + C} \cdot \tag{13}$$

The two general expressions for the phase difference as given by Eqs. (12) and (13) may now be applied to the four particular cases in the present problem. For air $\nu = 1$ and $\kappa = 0$.

The phase difference (δ_1) on normal reflection of the incident wave at the first metal is

$$\tan \delta_1 = \frac{2\kappa_1}{\nu_1{}^2 + \kappa_1{}^2 - 1} \cdot \tag{14}$$

As the wave enters the first metal from air the phase change (δ_2) is:

$$\tan \delta_2 = \frac{\kappa_1}{\nu_1{}^2 + \kappa_1{}^2 + \nu_1} \cdot \tag{15}$$

When the transmitted wave is reflected back into the first metal from the boundary surface between the two metals the phase change (δ_3) is given by the expression:

$$\tan \delta_3 = \frac{2D}{C^2 + D^2 - 1} \cdot \tag{16}$$

As the transmitted ray emerges from the first metal into air the phase change (δ_4) may be written:

$$\tan \delta_4 = \frac{-\kappa_1}{1 + \nu_1} \cdot \tag{17}$$

The phase change (δ_5) due to length of the optical path traversed by the transmitted wave passing twice through the first metal of thickness d is:

$$\delta_5 = \frac{2d}{\lambda'} \times 2\pi. \tag{18}$$

The total phase difference δ may be then written:

$$\delta = \delta_2 + \delta_3 + \delta_4 + \delta_5 - \delta_1. \tag{19}$$

EXPERIMENTAL RESULTS

The apparatus consisted of a sputtering chamber, a vacuum pump, synchronous rectifier and a one-half kilowatt 10 kv transformer. The sputtering chamber had a volume of about 2 liters. A small piece of glass ($\frac{1}{2} \times 2 \times 4$ cm) was placed in the chamber upon an inverted beaker with the receiving surface about 2 cm below the cathode. Usually a narrow strip of foil (silver, nickel or aluminum) was folded about the piece of glass, so that both glass and metal strip were sputtered at equal rates. Sometimes 2 or 3 strips of different metals were used simultaneously. Argon was used as a residual gas. The pressure in the chamber was kept constant at 0.04 mm which made the edge of the Crookes dark space tangent to the receiving surfaces. All metal parts (except the cathode) in the apparatus were made of aluminum. A piece of mica covered the receiving surface during a preliminary sputtering period. This was necessary in order to be able to adjust the pressure to the desired value and also to permit the cathode to warm up to a temperature at which the radiation losses equalled the heating effect of the discharge. This precaution is very necessary if one wishes to maintain a constant rate of sputtering. Preliminary measurements indicated that a 20 minute warming up period carried the temperature, of the particular cathode used, to 350°C at which thermal equilibrium was established. When steady conditions were obtained the mica was removed by an electromagnet device.

The time-record of the appearance of colors commenced at the instant of uncovering the receiving surfaces. It is impossible to assign a definite time of appearance for any particular color because the change of color is continuous and gradual. A record of the color was made at small intervals of time from which data one may select a "middle" value for the appearance of a particular color. The following table presents a partial typical record. In this case copper was sputtered upon glass and strips of nickel and aluminum simultaneously.

The rate of deposit of the copper was determined by weighing the glass before and after sputtering. Precautions were taken to reduce errors in weighing to a minimum. In the particular illustration the thickness of copper deposited per minute was found to be 3.8×10^{-7}cm.

In this record the glass also showed color changes. Yellow was first to appear and this occurred at 15 minutes. Following this it became purple at 20, blue at 25, and yellow again at 32 minutes.

Sputtering was continued for 2 hours and during this time color changes became weaker and uncertain due to the accumulation of copper upon the walls of the glass chamber.

In not all cases was the succession of colors as definite as that given in Table I. It is possible that the surface of the metal strips in such cases may not have been properly cleaned.

TABLE I. *Appearance of colors upon Ni and Al when sputtered by Cu.*

Time (min.)	Nickel	Aluminum	Time (min.)	Nickel	Aluminum
2.	Yellow	Yellow	18	Yellow	Yellow
3.25	Gold	Gold	20	Yellow	Bluish yellow
4.5	Purple	Dark gold	22	Light purple	Light purple
6.	Dark purple	Purple	25	Dark purple	Purple
8.	Blue	Pruple	30	Blue	Purplish blue
9.	Blue	Blue	33	Bluish green	Blue
11.	Lighter blue	Blue	37	Yellow	Blue
13.	Still bluish	Lighter blue	40	Yellowish purple	Bluish
16.	Yellowish	Yellowish blue	44	Purple	

One particularly interesting observation was that when the pressure in the sputtering chamber was lowered to 0.01 mm no colors, except perhaps a pale yellow, appeared. In this case the rate of sputtering was not determined but was more than 10 times as rapid as it was under a pressure of 0.04 mm. It is not clear why the color formation occurs at one pressure and not at another. The existence of the fact, however, indicates that there may be a critical pressure through which sputtering conditions change rapidly.

APPLICATION OF THEORETICAL CHANGE OF PHASE TO EXPERIMENTAL RESULTS

Change of phase for a copper film upon aluminum.

We assume, for the appearance of a yellow color when viewed in white light, that blue light (selected value $\lambda = 0.48\mu$) is eliminated by interference. The following numerical values of the optical constants for massive metals were taken from the International Critical Tables:

$$\text{Copper: } \nu_1 = 1.13,\ \kappa_1 = 1.96;\ \text{Aluminum: } \nu_2 = 0.93,\ \kappa_2 = 3.15$$

Substituting these values in Eqs. (14) to (17) gives:

$$\delta_1 = 43°30',\ \delta_2 = 17°23',\ \delta_3 = 30°35' \text{ and } \delta_4 = 137°20'.$$

Assuming that all of these changes of phase are in the same direction we find that $\delta_5 = 39°12'$, since δ must equal 180°. Reference to table 1 shows that a complete cycle of color change occurs in approximately 16 min. The time required to deposit sufficient metal to make $\delta_5 = 39°12'$ would be approximately 1/9 of 16 min. which is 1.8 minutes. The observed time for the first appearance of yellow is 2 minutes. This agreement is as good as could be expected.

Copper upon nickel.

Phase changes for a thin film of copper upon nickel were determined for appearance of a yellow color (interference produced in light for $\lambda = 0.46\mu$) by using the following constants for massive metals.

$$\text{Copper: } \nu_1 = 1.13,\ \kappa_1 = 1.92 \quad \text{Nickel: } \nu_2 = 1.46,\ \kappa_2 = 1.89$$

The calculated value of δ_5 was found to be $\pi + 110°$. Since $\tan(\pi+\alpha) = \tan\alpha$, we may assume that δ_1 was greater than that found by the formula by π. With this assumption $\delta_5 = 70°$ which would indicate that the yellow color should appear in 3.1 minutes. The observed time was 2 minutes.

These two illustrations may serve to indicate the character of confirmation obtained when using optical constants of massive metals. Fritze[4] has shown that the optical constants of metals vary also with the thickness of the sputtered film. When using his values of the constants for the thin metallic film, the calculated values of the change of phase did not agree with the experimental results.

Another test of the explanation given lies in an examination of the wave-lengths of light as determined by the thickness of the film. In the case of the deposition of a copper film upon aluminum or upon nickel the color cycles are of approximately the same length of time in each of the two cases. This fact substantiates interference.

We may also use the wave-length of a particular color to determine the thickness of the film. Using the index of refraction ($\nu_1 = 1.13$) of copper for $\lambda = 0.48\mu$ gives a value of 0.425μ for the wave-length in copper and for the thickness of the film a value of 0.212μ. Since a complete cycle of color change occurs in 16 min. (Table I) the thickness of the film is 0.0608μ. This latter value is approximately one-third of the former. The discrepancy is too large to be explained by possible errors in weighing the films, although it is possible that the rate of sputtering changes after the first few minutes of sputtering under the conditions of the experiment. The result given here is confirmed by a similar lack of agreement when sputtering other metals.

In conclusion it may be stated that the experimental evidence partially confirms the explanation of the colors of thin sputtered films as due to interference.

The writer wishes to express his appreciation of the services of Mr. Robert Wathen and Mr. Maxwell Kelch for their assistance in making experimental observations.

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[4] Fritze, Ann. d. Physik **47**, 763 (1915).