THE HALL EFFECT AND SPECIFIC RESISTANCE OF CATHODICALLY DEPOSITED FILMS OF GOLD

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ABSTRACT

Hall coefficient for sputtered films of gold was determined for films varying in thickness from about 10 mμ to 80 mμ, and was found to be independent of the current (even though current densities up to 10^6 amp./cm^2 were used), of the magnetic field (3 to 28 kilogauss), and of the thickness (computed from the surface density), and of previous treatment of the film, and to have the same value as for bulk metal, 643×10^{-6}. This is accurate to one per cent since the high current densities used gave e.m.fs. of over a milli-volt. The constancy of the coefficient agrees with the theory that the sputtered particles have individually the same properties as the bulk metal.

Specific resistance of sputtered films of gold is erratic for films less than 10 mμ thick, but for thicker films is proportional to $\rho/(\sigma-\sigma_0)$ where σ is surface density and ρ is the density. The specific resistance r came out about 3 times the value for bulk metal. The high value is doubtless due to poor electrical contact between particles. From the value of the constant σ_0, 20×10^{-6} gm/cm^2, the average size of the particles is of the order of 10^{-6} cm.

THE Hall effect of thin films has been studied by Kundt,[1] Moreau,[2] Wait,[3] and Steinberg.[4] Kundt used electrolytically deposited films of the ferro-magnetic metals. Moreau used chemically and electrolytically deposited films of silver and nickel. He found that the Hall coefficient varied with the thickness and explained his results on the transition layer theory suggested by Vincent.[5] Wait used chemically deposited films of silver, and found that the Hall coefficient was constant, independent of the thickness and had the same value as metal in bulk, for thicknesses as low as 23 mμ. Steinberg obtained his films by evaporation in a vacuum. In the case of silver and copper he found the Hall coefficient to be less than that for the bulk metals, and in the case of the iron films about five hundred per cent greater.

As far as is known, no previous attempt has been made to determine the Hall coefficient in the case of films obtained by cathodic sputtering.

[1] Kundt, Weid. Ann. **49**, 257, 1893
[2] Moreau, J. de Phys. **10**, 478, 1901
[3] Wait, Phys. Rev. **19**, 615, 1922
[4] Steinberg, Phys. Rev. **21**, 22, 1923
[5] Vincent, J. de Phys. **9**, 78, 1900

Apparatus and Procedure

The sputtering apparatus was of the usual form. The high potential was obtained by a half kilowatt 10,000 volt transformer, with a kenetron in series. The use of the kenetron eliminated the heating effect due to the reverse current, and allowed more rapid sputtering. The current was maintained at 15 milli-amperes. The vacuum was obtained with a rotary oil pump and a Gaede molecular pump in series. The pressure was measured on a McLeod gauge and the sputtering was all done at a pressure of about 30 μ, the residual gas being air.

The films were deposited on square glass plates that were approximately 12 cm on a side. The cathode was a square piece of commercially pure gold 12 cm on a side. The terminals were first deposited by sputtering dense films of gold as shown in Fig. 1a. The mask used to protect the rest of the film is shown in Fig. 1b. The film to be studied was then

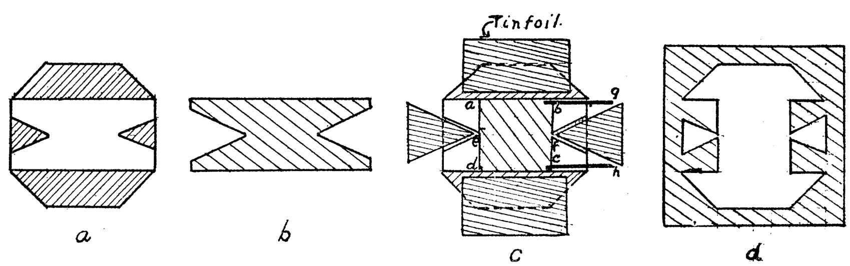

Fig. 1. Shields used in sputtering.

deposited so as to overlap the terminals. The film used in studying the Hall effect, is indicated as *abcd*, in Fig. 1c. It was square, 7 cm on a side. The mask used in sputtering this film is shown in Fig. 1d. Contact to all four terminals was made by cementing thereon tin foil with "Clamping Paste," kindly furnished by the General Electric Company. A spectrophotometric test showed no difference in uniformity of the deposit. The film, ready for mounting, is shown in Fig. 1c. Additional terminals were connected to the top and bottom of the film (g and h in Fig. 1c) in order to measure the resistance by the potentiometer method, thus eliminating any error due to poor or variable contacts. The side terminals e and f were adjusted by scraping with a knife so that they were at the same potential when current was flowing through the film and no magnetic field was present.

In the case of film as thin as those used in this study, the term thickness loses its usual meaning, and it seems desirable to speak of mass per square centimeter, which will be called "surface density" hereafter. Both the Hall coefficient and the specific resistance can be expressed as significantly and as clearly in terms of this surface density as of thickness. In order, however, to enable comparison with other work, the term thickness will be used in places, and it should be understood that it is used in the sense of average thickness, and is determined by dividing the mass per square centimeter by the density of gold in bulk, taken to be 19. The films studied varied in thickness from approximately 10 mμ to 80 mμ.

The surface density of these films was determined in the following manner. Thin sheets of mica, having an area of about 40 cm^2 were weighed on an assay balance, sensitive to .01 mg, before and after sputtering. A piece of glass, similar to those on which all the films were deposited was placed beside the mica in the sputtering jar during the sputtering and received, presumably, the same thickness of film as the mica. The transmission of blue light, ($\lambda = 5000$ A), by both the film on the glass and that on the mica were then measured with a spectrophotometer.

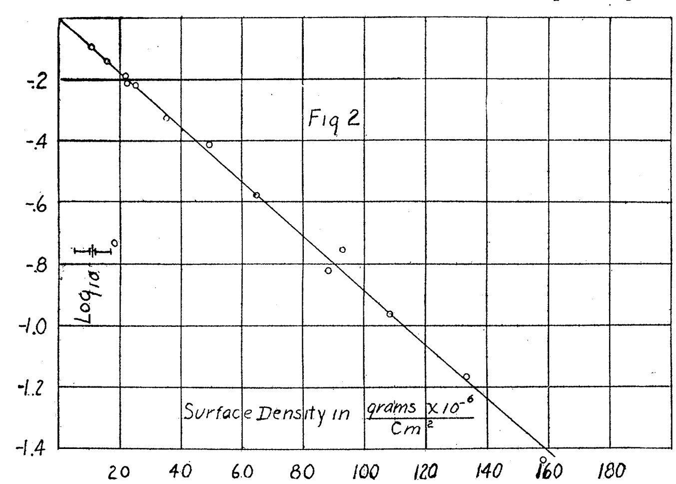

Fig. 2. Transmission of light as a function of surface density.

Since the transmission of this same frequency was determined before sputtering for both the glass and mica, the intensity of the incident light could be corrected for the light reflected or absorbed by the glass and mica. On making this correction concordant values for the transmission of the two films were obtained in each case. For a series of such films of varying thickness, it was found that if the logarithm of the ratio of the light transmitted to the incident light (log I/I_0) was plotted against surface density, a straight line going through the origin was obtained. This curve is plotted in Fig. 2. By measuring the intensity of light transmitted by the films used in determining the Hall coefficient, correcting for the loss of light due to reflection from the glass surface which was found to be eight per cent, the surface density of these films could be readily determined from the curve.

This curve is not corrected for the difference in the reflecting power between a glass-air and glass-gold surface. This will not affect the accuracy of the determination of the surface density, since the same procedure was used in determining the curve as in using it to obtain the surface density.

The Hall electromotive force was measured by a potentiometer. Current was sent through the film only while a balance was being made. A number of readings of the potentiometer were taken for each value of the resistance, in order to minimize any thermal electromotive forces and any differences in potential between the side terminals due to changes in the resistance of the film from heating. Sufficient resistance was kept in series with the film so that any change of its resistance due to heating would not affect the value of the current to any appreciable extent. By taking these precautions, it was possible to use large values for the current, with a resulting increase in accuracy in measuring the Hall electromotive force. In measuring the Hall effect the film was mounted rigidly in a suitable wooden frame, attached to one of the pole pieces of the magnet.

The magnet used was made by the Société Genevoise and was water cooled. In most cases the pole pieces were cylinders 10 cm in diameter, and these were kept at a distance of 0.9 cm apart in order to obtain as uniform a field as possible. The value of the field was determined by a flip coil and a standard mutual inductance in series. The current in the primary of the mutual inductance was adjusted until the same throw of a ballistic galvanometer was obtained on breaking this current as by removing the flip coil from the field. The ballistic galvanometer was used simply as an indicating device and its constants did not enter into the computations of the field strength.

Experimental Results

Hall Effect. The Hall coefficient was found to be independent of the current, magnetic field strength, and thickness in all the films studied. The Hall electromotive force E is usually represented by the formula

$$E = RHI/t$$

where R is the Hall coefficient H the magnetic field strength, I the current, and t the thickness. If surface density is used in place of thickness,

$$E = R'HI/\sigma$$

where σ is the surface density, and $R' = R\rho$ where ρ is the density of the metal.

The proportionality between the Hall electromotive force and the current is shown in Fig. 3. This proportionality was found to hold for very large current densities. On account of the large surface for radiation, it was possible to use current densities as high as 10^6 amp. per cm.[2] These results would indicate that the Hall coefficient is independent of the current, and does not show any saturation effect. On account of the extreme thinness and the large current densities, the Hall electromotive

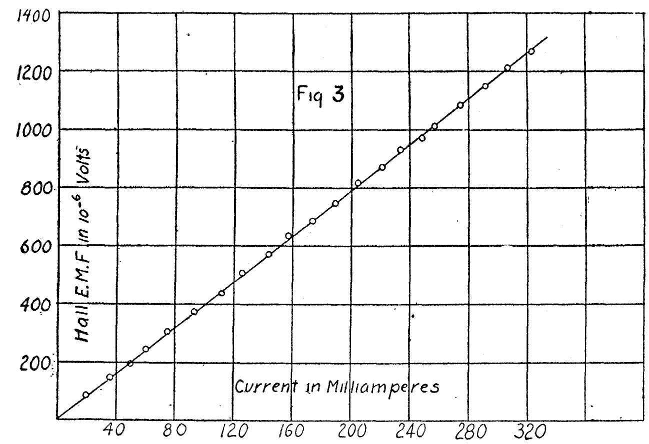

Fig. 3. Hall e.m.f. as a function of current.

force is very much greater than can be obtained in metal in bulk, and the accuracy of measuring it is consequently much greater.

The proportionality between the Hall electromotive force and the magnetic field strength is shown in Fig. 4. This curve is for a film having

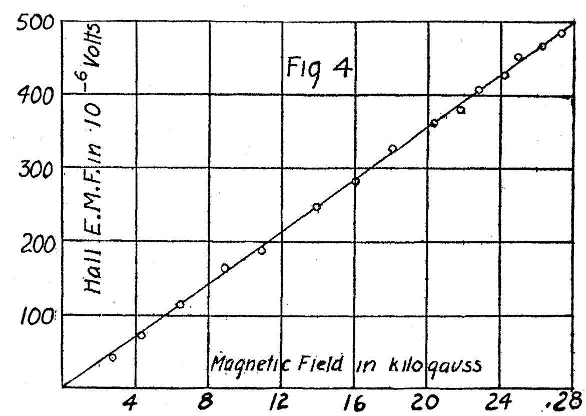

Fig. 4. Hall e.m.f. as a function of magnetic field.

an area of about 6 cm² and smaller pole pieces were used in order to investigate the effect at high values of the field strength. No difficulty was experienced in measuring the Hall electromotive force for field strengths ranging from about 3 to 28 kilogauss.

The relation between the Hall electromotive force and surface density was determined for films having an average thickness ranging from about

10 mμ to 80 mμ. Curve 1 in Fig. 5 shows the Hall electromotive force plotted against the reciprocal of surface density. This curve represents an average of practically all the measurements of the Hall effect. The values of E/HI plotted as ordinates were determined from the slopes of curves similar to that shown in Fig. 3, and each point represents the average of a great number of readings taken at different values of the current and field strength. The ordinates of this curve are in c.g.s. units. If we assume an average value of 19 for the density of the films,

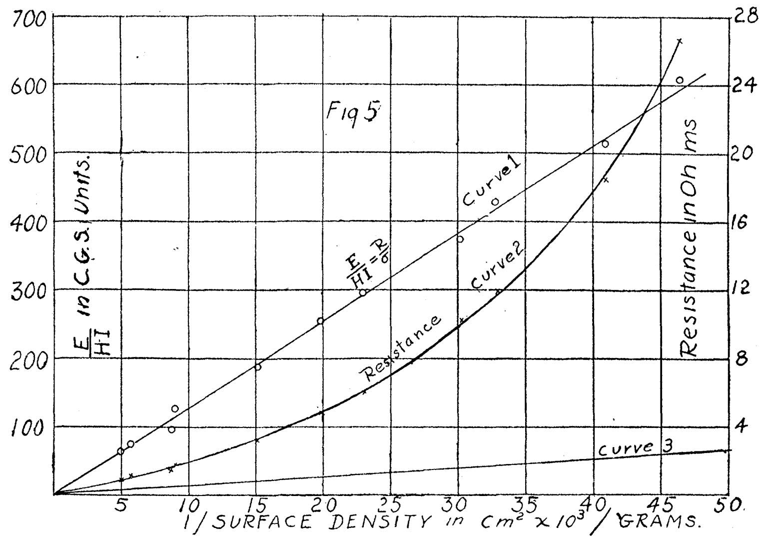

Fig. 5

Curve 1: Hall e.m.f. divided by HI as function of reciprocal of surface density.
Curve 2: Resistance of films.
Curve 3: Resistance of bulk metal.

the value of the Hall coefficient, expressed in terms of the thickness, determined from this curve is 643×10^{-6}. The value of the Hall coefficient determined for the bulk metal ranges from 570×10^{-6} to 710×10^{-6}.

The Hall coefficient was found to be independent of the previous history of the films. Measurements made directly after sputtering gave the same value for the Hall coefficient as measurements made after heat treatment and also as measurements made after the films had stood for two months exposed to the air. In fact, the Hall coefficient was not changed by any treatment that did not noticeably injure the film. This is in marked contrast to the behavior of the resistance of these films and also to the change of resistance in a magnetic field in the case of bismuth films.[6]

[6] Curtis, Phys. Rev. **18**, 255, 1921

It is well known that the resistance of sputtered gold films increases enormously for thicknesses less than about 10 mμ.[7] Attempts to obtain reliable data on the Hall effect with these very thin films were not successful on account of the large change in resistance of the films during measurement. The potential between the side terminals would change so much that the relatively small change due to the Hall effect was masked. This is evidently due to the fact that the resistance of the films changed as current was sent through them, and the resistance did not change uniformly all over the surface. Although these films appeared uniform to the eye, the points of equipotentials on the two sides, when current was sent through the film with no magnetic field present, was not, in general, at the midpoints of the two sides, and the location of these points of equipotential seemed to change every time current was sent through the film. Another difficulty in measuring the Hall effect of these very thin films is that as the resistance is very high, only a small current could be sent through the films without unduly heating them. Consequently the magnitude of the Hall electromotive force was greatly reduced. From such data as could be obtained, however, no evidence was obtained that the Hall coefficient changes for these films, although the specific resistance increases to several hundred fold its value for bulk metal.

Specific resistance. The resistance and the change in resistance in sputtered films has been studied by many observers, among whom may be mentioned Miss Stone,[8] Patterson,[9] Swann,[10] Pogeny,[7] King,[11] and Koller.[12] The results of the present work are in agreement with the results previously reported. Values for the resistance of films less than 10 mμ will not be included in this report, for the resistance is so unstable for these very thin films that elaborate precautions are necessary to make the data trustworthy, and these precautions were not taken. The value of the resistance of those films on which the Hall effect was studied is given, as the resistance of these films after aging at 150°C for two hours is quite constant. Over a long period of time, however, the resistance of these films would change by several per cent. The curve between the resistance and the reciprocal of the surface density is shown in Fig. 5, Curve 2. Curve 3 is the curve that would have been obtained if the specific resistance of the films had been constant and had had the same value as that for gold in bulk.

[7] Pogeny, Phys. Zeit. **15**, 563, 1914
[8] Miss Stone, Phys. Rev. **6**, 1, 1899
[9] Patterson, Phil. Mag. **4**, 652, 1902
[10] Swann, Phil. Mag. **28**, 467, 1914
[11] King, Phys. Rev. **10**, 291, 1917
[12] Koller, Phys. Rev. **18**, 221, 1921

Discussion of Results

The work of Smith,[13] Wold,[14] Lebret,[15] and others would indicate that the Hall coefficient depends, at least in part, on the crystal structure of the metals. Wait[3] has shown that the Hall coefficient should be the same for films consisting of groups of crystals as for the metal in bulk, even though these particles are not in as intimate electrical contact as in the bulk form. The results of this study seem to confirm the theory that these films consist of particles of the same crystal structure as that obtaining in the bulk form.[16] The films will therefore be considered as consisting of particles, or small crystals, which have, individually, the same properties as the bulk metal, arranged at random on the surface of the glass.

When the surface of the glass is only partly covered by these particles, there are individual particles as well as groups of particles that do not make electrical contact with the other particles deposited. In this state the addition of a relatively few particles may decrease the resistance greatly as they may serve to establish electrical contact between large groups of particles. The resistance would be a complicated function of the number, size and physical condition of the particles.[17] Under these conditions, the resistance would be unstable since contacts might easily be made and broken between groups of these particles by heat. Since the resistance of the films used in this study was practically constant, it is probable that the surface is practically covered and that all the particles are in electrical contact. It is interesting to consider how the resistance, or preferably the conductivity, will depend on the number of particles deposited, when the surface is practically covered.

Consider a film in this state. All the particles are touching other particles. If the particles have fallen at random, according to the law of probability, the surface is not covered to a uniform depth and all the particles will not be equally effective in conducting an electric current. If now an additional number of particles ΔN are added, the additional number of particles that will be made effective in conducting the current will be ΔN, since the contour of the surface will, on the average be the same.

If K is the conductivity,

$$dK = k_1 dN$$
$$K = k_1(N - N_0)$$

[13] Smith, Phys. Rev. **10**, 358, 1917; Phys. Rev. 17, **37**, 1921.
[14] Wold, Phys. Rev. **7**, 169, 1916
[15] Lebret, Leid. Com. 119, 1895.
[16] Kahler, Phys. Rev. **17**, 210, 1921
[17] Koller, loc. cit.[12]

where N_0 is the equivalent number of particles that are ineffective in conducting the current due to the roughness of the surface. Since the number of particles is proportional to the mass per square centimeter

$$K = k(\sigma - \sigma_0)$$

In Fig. 6, the conductivity is plotted against the surface density, and it is seen that the above equation is satisfied by the data, except at small values of the surface densities. Actually the curve is as shown and joins the x axis at a surface density of about 6×10^{-6} grams per square centimeter. The value of the constant k gives the specific conductivity

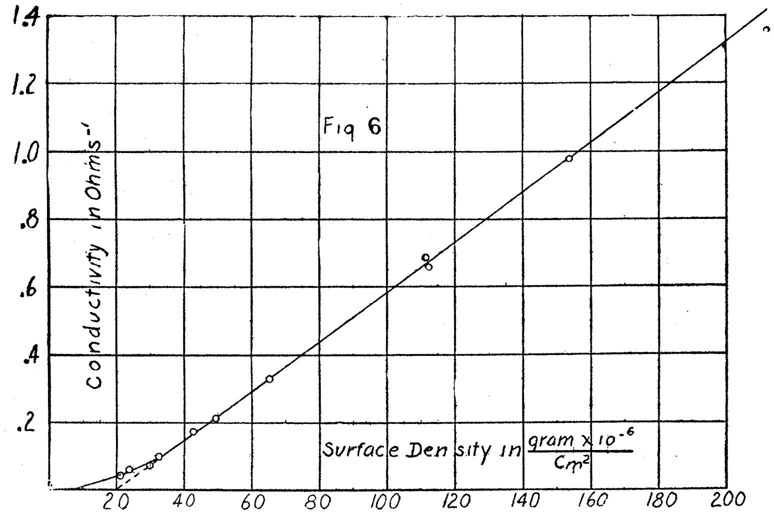

Fig. 6. Conductivity as a function of surface density.

in terms of grams per square centimeter. This is about .35 of the value of the specific conductivity for gold in bulk. This difference is probably due to the gas absorbed by each particle which prevents the particles from making good electrical contact.[18]

From this curve between the conductivity and the surface density it is possible to obtain a rough approximation of the size of the particles. If we assume that the particles are all the same size, the intercept on the x-axis can be shown to be equal to the surface density of a single layer of particles, completely covering the surface. Dividing 20×10^{-6} by the density of gold 19 we get 10^{-6} cm as the average thickness of the particles.

In conclusion the writer wishes to express his thanks to Professor F. K. Richtmyer for his constant help and encouragement throughout the work.

CORNELL UNIVERSITY,
August 7, 1923

[18] Kohler, loc. cit.[12]