THE ELECTRICAL CONDUCTIVITY OF SPUTTERED FILMS.

BY ROBERT W. KING.

IT has been known for a long time that the specific resistance of the very thinnest metal films is abnormally high.[1] Two theories have been advanced to explain this fact; one by J. J. Thomson[2] depends upon a shortening of the mean free path of the conducting electrons by the surface of the film; the other by Swann[3] depends upon an assumed granular structure of the film and consequent opposition offered to the motion of the electrons by the gaps between the grains.

Swann[3] has raised one objection to Thomson's theory. Another has developed as a result of the present work. Thomson gives as the expression for the mean free path of an electron in a film

$$\lambda' = t\left(\frac{3}{4} + \frac{1}{2}\log\frac{\lambda}{t}\right), \qquad t < \lambda,$$

λ being the mean free path for the metal in bulk, and t being the film thickness. Evidently λ' varies less rapidly than the first power of t; and since the specific conductivity, other things being the same, is probably proportioned to λ,' we find that the specific conductivity of a film should vary less rapidly than the first power of t. This, however, is certainly very seldom if ever the case. The writer finds this exponent, instead of having a value less than unity, to have values ranging between 10 and 50, and sometimes reaching as high as 200.

Swann's theory, on the other hand, seems open to at least two objections. First, it is difficult to picture the mechanism by means of which in all cases the grains of the film are distributed so as to lie separated from one another by gaps of practically uniform width. The natural supposition would appear to be (as indeed Swann suggests) that of a more or less random distribution, in which certain grains would undoubtedly touch some of their neighbors and be quite distantly separated from others. When two grains actually touch, it would seem reasonable to suppose

[1] I. Stone, PHYS. REV., 6, 1, 1898. Vincent, Ann. de Chin. et de Phys. (7), 19, 494, 1900. Longden, PHYS. REV., 11, 40, 1900. Patterson, Phil. Mag. 4, 1902.

[2] J. J. Thomson, Cambr. Phil. Proc., 11, 120, 1901.

[3] W. F. G. Swann, Phil. Mag., 28, 467, 1914.

that the resistance of their contact is not abnormally high. Second, the effect of such gaps between grains, as Swann imagines would, on the whole, be to lengthen the mean free path of the electrons above the value holding for those in the metal in bulk. This in turn should make the resistance of the film more than usually susceptible to the action of a transverse magnetic field. Such a susceptibility the writer has however failed to find in films of either platinum, gold or silver.[1]

The following is an attempt to put the supposition of a random distribution[2] of grains into a quantitative form. Imagine the points of Fig. 1 to represent the centers of the metallic grains. The components of all pairs of these points which lie less than a certain distance apart have been joined. The result is the formation of complicated net-like paths over which it will be supposed conduction can occur. The problem is to express the total conductivity of these paths as a function of the number of particles composing the film.

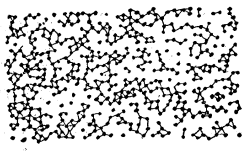

Fig. 1.

Let c represent the conductivity of the film, N the total number of grains per unit area, and n the smaller number through which conduction can occur. Since the n grains which constitute the conducting paths must, taking the film as a whole, be practically uniformly distributed, we may suppose

$$n = cf(N),$$

where $f(N)$ is a function which may be expected to decrease slightly in value as the conducting paths become greater in number and consequently straighter. Now consider the effect of increasing N by the addition dN. The fraction $cf(N)/N \times dN$ of these particles will on the average evidently become conducting particles. But as a result of the addition, other particles from among the $N - n$ already upon the film will change over to the conducting kind; and it probably is quite safe to assume that the number which make this change is proportional to the number added $cf(N)/N \times dN$. That is, each particle which, when added, is of the conducting kind, will on the average enable four or five or some other number ρ of the $N - n$ particles to change to the conducting class. This number ρ must of course vary some with N; particularly will this be so as N gets so large that the grains of the film begin to form more than one layer, in which case it will tend toward zero. But we can doubtless say

[1] It might be recalled here that Patterson (*l. c.*) obtained similar results for platinum and silver, and that for bismuth he found the change of resistance to be noticeably less for a film than for the metal in bulk.

[2] It should be borne in mind that the distribution of grains cannot be random in the sense that a distribution of points might be random, since the grains have an appreciable size.

that throughout a certain portion of the development of the film, ρ will remain constant. Then, since

$$dn = cdf + fdc = (\rho + 1)\frac{cfd}{N}N,$$

we have

$$\frac{dc}{c} + \frac{df}{f} = (\rho + 1)\frac{dN}{N},$$

or

$$\log c + \log f = (\rho + 1)\log N + \text{const.}$$

As pointed out above, the variation of $f(N)$ is likely to be slight in any case. Let us suppose it constant. Then

$$\log c = (\rho + 1)\log N + \text{const.},$$

which is a relation agreeing very well with experiment.

EXPERIMENTAL PROCEDURE.

The vacuum tube in which the sputtering was done presented no noteworthy features except that it was provided with a pair of wires, leading from the film to the exterior, by means of which the resistance of the film could be measured *in situ*. Each film was approximately 1×1.5 cm. and was deposited upon a piece of glass immediately after two dense patches of film to serve as contacts had been deposited. Before beginning the film, the discharge was run for a period varying from a few minutes to half an hour, depending upon the metal used as cathode; and during this preliminary discharge the plate of glass was protected by a cover of glass. After conditions within the tube appeared to have become steady, the discharge was stopped and the cover glass slid away by tilting the tube.

The deposition of the film was now carried out in small stages. In the case of platinum and silver, the interval used was two seconds, while for gold one second seemed more suitable. These periods of deposition were accurately timed by means of a slowly falling piston, the piston being released by the starting of the discharge, and it in turn stopping the discharge upon reaching the bottom of its fall. The discharge was obtained from an induction coil operating on an alternating current, one half of each secondary wave being suppressed by a kenetron in series with the coil and tube.

At the end of each interval of deposition, the conductivity of the film was tested for or measured. The measurements were carried out by noting the current which a known potential difference would send through the film and a sensitive galvanometer placed in series. The resistance of the galvanometer was enough smaller than that of the films

to make correction for it unnecessary. The greatest resistance measured was about 1.4×10^{11} ohms.

The data of Table I. are typical of the values obtained for gold, silver and platinum.

TABLE I.

Gold.		Silver.		Platinum.	
Time.	Conductivity.	Time.	Conductivity.	Time.	Conductivity.
31 sec.	$3.4\times10^{-10}\frac{1}{\Omega}$	80 sec.	$7.1\times10^{-12}\frac{1}{\Omega}$	10 sec.	$2.2\times10^{-11}\frac{1}{\Omega}$
32	4.6×10^{-9}	84	9.6×10^{-11}	14	8.9×10^{-10}
33	4.2×10^{-8}	88	1.8×10^{-9}	18	12.2×10^{-9}
34	3.9×10^{-7}	92	1.6×10^{-8}	22	10.3×10^{-8}
35	2.9×10^{-6}	96	1.6×10^{-7}	26	6.4×10^{-7}
37	2.7×10^{-5}	100	1.1×10^{-6}	30	2.1×10^{-6}
39	4.8×10^{-5}	104	3.4×10^{-6}	34	3.9×10^{-6}
41	5.7×10^{-5}				

The accompanying curves, with the exception of Fig. 6 show to what extent films of platinum, gold and silver agree with the relation given

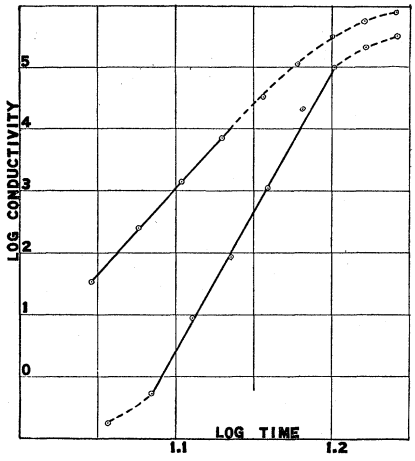

Fig. 2.

Curves for platinum obtained by sputtering in a large bell-jar.

above.[1] The films of platinum giving the curves of Fig. 2 were sputtered in a large bell-jar having about three times the capacity of the vacuum tube used in making all the other films. Otherwise conditions were as nearly as could be judged the same.

It is evident from the curves that ρ stays constant for a greater range

[1] In plotting these curves it has been assumed that N is proportional to the time of sputtering.

of values of the conductivity in the cases of platinum and gold than in the case of silver. However, the deviations of the curves for silver may be partly due to the difficulty experienced in keeping the conditions within the tube constant when using a silver cathode.

Computing the range of values of N throughout which ρ remains con-

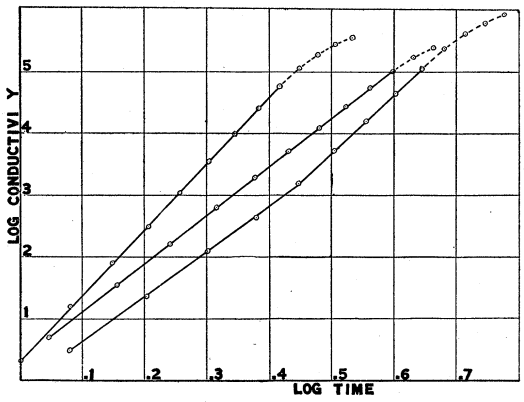

Fig. 3.

Curves for platinum obtained by sputtering in a small bell-jar.

stant brings to light peculiar differences. Table II. gives average values of the ratio $\Delta t/t_0$, t_0 being the time during which deposition must occur in order that the film just show a measurable conductivity, and Δt the time from the beginning of conduction to the end of the straight portion of the curves. The corresponding values of ρ are also given.

TABLE II.

Metal.	$\Delta t/t_0$.	ρ.
Pt I.	0.35	45
Pt II.	2.40	7
Au.	0.26	60
Ag.	0.32	40

The variations of ρ and $\Delta t/t_0$ among the various films are probably due to different degrees of regularity of arrangement of the grains. If for some reason the arrangement in a given film is very regular, it would be likely to cause a large value of ρ and small value of $\Delta t/t_0$. This point as well as a possible explanation of the difference between platinum I. and II. will be returned to presently.

The lowest point on each of the curves for gold does not have much significance. Gold films, when they first begin to conduct, seem to undergo

a rapid growth of conductivity without the addition of any metal. For example, the film from which Curve 5 was plotted, when first observed after 31 seconds deposition, had a conductivity so small as to be scarcely measurable. At the end of about a minute, this had increased over a hundred-fold to the value plotted, and even then was increasing slowly.

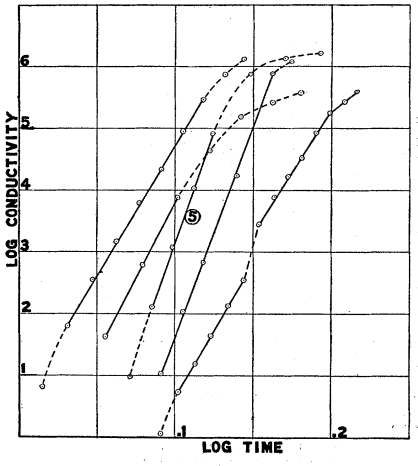

Fig. 4.
Curves for gold.

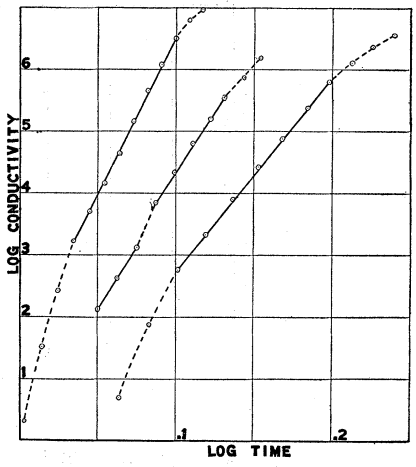

Fig. 5.
Curves for silver.

This spontaneous increase, however, rarely if ever put in an appearance after the next addition of metal. Neither platinum nor silver showed ageing to a detectable extent, although it is likely they would have done so had the time of observation been lengthened sufficiently.

No effort has been made to measure the actual thicknesses of the various films. Certain limits can however be set with a fair degree of accuracy. The films of platinum at the conclusion of deposition were still so thin that, when looked at through the glass slide, they appeared as dark patches on a bright background, this being due to the fact that the reflecting power of the surface between glass and film was less than that between glass and air. The gold and silver films were thick enough to make their reflecting powers on the glass slide about equal to that of a clean glass surface. From these facts, and making allowance roughly for the variation of optical constants with film thickness,[1] it is probably safe to conclude that the final thicknesses lie between 6 and 10$\mu\mu$, the platinum films being somewhat the thinnest.

These values of the thickness give a rough indication of the average size of the particles for the different metals. As mentioned above, gold

[1] W. Planck, Phys. Zs., 15, 563, 1914. B. Pogany, Phys. Zs., 15, 688, 1914.

and silver films did not as a rule show any conductivity until about three fourths of the final amount of metal had been deposited. Platinum films (II.), on the other hand, began to conduct after about one third of the final amount of metal had been deposited. We may therefore say that a platinum film, in order to just show conduction, must have an average thickness between 1.5 and 3 $\mu\mu$, while gold and silver films have an average thickness between 6 and 8 $\mu\mu$. Doubtless the average sizes of the particles for the differet metals are considerably in excess of these thicknesses.

Direct evidence as to the existence of these particles has been obtained. Various investigators have examined films microscopically, but with the exception of Houllevique[1] have failed to detect any signs of structure. Houllevique records that a film of silver about 10 $\mu\mu$ thick when examined with a magnification of about 1,300 diam. appeared continuous but granular. It occurred to the writer to try a "dark field" microscope. In this instrument, films of gold and silver, of such thicknesses that they would be on the straight portions of the curve, show an unmistakable granular structure; for somewhat thicker films, the granular structure has almost if not entirely disappeared. On the other hand, no detail of any kind could be observed in platinum films; but as was indicated above, the size of the platinum grains is probably considerably smaller than those of gold and silver, and they were quite likely without the range of the microscope.

This instrument had a magnification of about 500 diam., a power too low to make it feasible in any but a few cases to estimate the average distance between particles. One of these was that of a gold film which probably consisted of almost enough metal to enable it to conduct. The average distance between particles seemed about 500 $\mu\mu$. Of course this gives no indication of the actual size of the particles.

The question naturally arises as to how these particles are formed. It certainly is not easy to conceive of them as being detached as units from the cathode by the positive ion bombardment. It seems much more reasonable to think of the cathode as losing particles of practically atomic size, these uniting later to form the larger agregates.[2]

This view receives striking support through a comparison of the writer's data with those recently published by Weber and Oosterhuis concerning films produced by evaporation. Such films, it is known, are built up by the condensation of atoms. These investigators find that a platinum film in order to just conduct must be about 1.5 $\mu\mu$ thick, and a silver film must

[1] L. Houllevique, Cr., 148, 1320, 1909.

[2] Cf. Longden and Houllevique, *l. c.*

be about 6 $\mu\mu$ thick. The almost exact agreement of these values with those obtained by the writer can scarcely be considered accidental, but would seem rather to be due to the films having been made by essentially the same process.

Nor does the similarity between the two sets of data end here. Fig. 6

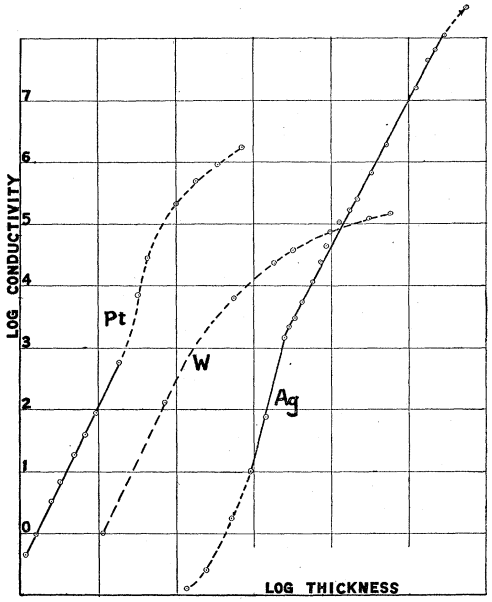

Fig. 6.

shows the result of plotting the values of Weber and Oosterhuis in accordance with the equation

$$\log c = (\rho + 1) \log t + \text{const.}$$

The agreement in the cases of platinum and silver is very nearly as good as that given by the writer's data, while the case of tungsten is indefinite. These facts therefore make it seem likely that in sputtering, the metal leaves the cathode in about the same condition as if it were evaporated at high temperature, so far as the writer is aware, there are no facts to which such a view runs counter.

Now since metallic atoms and small clusters of atoms display a marked tendency, even at ordinary temperatures, to merge together when brought sufficiently close, the particles found in sputtered films are readily accounted for. But the process of condensation may occur at different stages; entirely during the passage of the dark space, or entirely upon reaching the glass, or partly in each place. The stage at which it occurs

for any particular film doubtless depends upon the conditions of vacuum and discharge as well as upon the metal used as cathode. And it seems likely that the manner of growth of the conductivity of any particular film would in part be determined by the condition of the metal at the instant of deposition,—whether it is in fully formed aggregates, or in atoms or small clusters which are to unite with one another to a greater or less extent after striking the glass. In this way a possible explanation is formed of why the values of ρ and $\Delta t/t_0$ differ so materially for the platinum films of Figs. 1 and 2.

A satisfactory theory of film structure must account for the optical as well as the electrical peculiarities. W. Planck and B. Pogany (*loc. cit.*) have recently measured the indices of refraction and coefficients of absorption of sputtered platinum and copper films. They find certain variations which they propose to account for by an assumed shortening of the electronic mean free path. But it should be pointed out that their values are quite similar to those Garrett[1] has shown would be expected on the basis of a granular structure, and are therefore in accord with the theory here presented.

The question of a negative temperature coefficient has not yet been investigated, but the writer considers it likely that this phenomenon will find an adequate explanation in terms, partly of a differential expansion between glass and film, and partly in terms of the remarkable tendency to unite which minute particles of metal show even at ordinary temperatures.

In conclusion the writer wishes to thank Professor F. K. Richtmyer for his help and constant interest. He also wishes to acknowledge assistance from the Rumford Fund for the purchase of apparatus.

SUMMARY.

1. Reasons are given for rejecting Thomson's and Swann's theories of the abnormally small specific conductivity of metal films.

2. A relation connecting conductivity and thickness is deduced from the supposition of a more or less random arrangement of groups of atoms. This relation seems to fit observations upon films of platinum, gold and silver in a very satisfactory manner.

3. It has been found that the thinnest films of gold and silver show a granular structure when examined with a " dark field " microscope, and that thicker films of these metals appear quite uniform. No structure has been observed in platinum films, but this is probably due to the limitations of the microscope.

[1] J. C. M. Garrett, Phil. Trans., A, Vol. 202.

4. It has been found that in order to just conduct, platinum films must be between 1.5 $\mu\mu$ and 3 $\mu\mu$ thick, gold and silver films between 6 $\mu\mu$ and 8 $\mu\mu$ thick. As it seems doubtful if particles of the sizes necessitated by these thicknesses can be detached from the cathode by the bombardment, their formation is probably due to the condensation of atoms of the metals. This supposition is further supported by the similarity between the writer's results and those of Weber and Oosterhuis obtained on films produced by condensation.

5. It is pointed out that the recorded variations of n and k with thickness appear to present no obstacles to the acceptance of the present theory.

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