PHYSICAL PROPERTIES OF THIN METALLIC FILMS.[1]

III. SOME FACTORS AFFECTING THE RESISTANCE OF SPUTTERED PLATINUM FILMS.

BY LEWIS R. KOLLER.

SYNOPSIS.

Resistance of sputtered platinum films; aging in vacuo and in various gases.—The rapid decrease of resistance which occurs if a film is kept in vacuo after sputtering, is doubtless due to coalescence or agglomeration of the particles making up the film. In air, oxygen and hydrogen, however, this aging practically stops, probably because the adsorption of gas around the particles prevents further coalescence until the gas is removed by reëvacuation or by chemical means. This adsorption theory was tested in various ways and was found in accord with all the facts. Nitrogen and carbon dioxide are only slightly adsorbed. The *effect of heating* is to accelerate and further the aging process but with prolonged heating the resistance reaches a minimum and then increases indefinitely. *Temperature coefficients of resistance* to 200° C. were measured for films previously aged at a higher temperature and were found to depend, like the resistance itself, more on the physical condition, as determined by heat treatment, than on the thickness of the film. The highest coefficient measured was 0.002 which is about 4/7 of that of platinum in bulk. Very thin films have negative coefficients.

Activation of platinum by sputtering.—Both the sputtered film and the cathode used in sputtering cause hydrogen and oxygen to combine at room temperature so rapidly that the film and the cathode may become very hot.

HISTORICAL SUMMARY.

ONE of the most noticeable properties of thin metal films, deposited by cathode sputtering, is that they undergo a change in resistance with time. For some metals this change is an increase, for others it is a decrease, while some pass through a minimum. In general the change is accelerated by heat. This process of change in resistance with time has been called aging.

These facts have been observed by several investigators. Kohlschutter and Noll[2] found that silver films at first decrease in resistance with time after sputtering and then increase, the manner of this change depending on the nature of the film as determined by the gas in which it was sputtered and on the heat treatment which it received after sputtering. Patterson[3] found that bismuth films increase in resistance after

[1] The writer is pleased to acknowledge assistance from a grant from the Rumford Fund to Prof. F. K. Richtmyer.

[2] Kohlschutter and Noll, Zeit. fur Elektrochemie, 18, 419, 1912.

[3] Patterson, Phil. Mag., Series 6, *4*, 652, 1902.

sputtering, and that platinum films decrease in resistance on heating. Longden's[1] results were similar to those of Patterson. Miss Hobbs,[2] also working with platinum, found that the films decreased in resistance when allowed to age in vacuo, but rose in resistance when air was admitted to the sputtering jar.

It was the purpose of this investigation to study the aging of sputtered films, particularly with reference to the effect on aging of adsorbed gases. Unless otherwise specified the films studied were of platinum.

DESCRIPTION OF APPARATUS AND PROCEDURE.

The sputtering apparatus was of the type usually used for this purpose and needs no special description. The high vacua when required were obtained with a Langmuir pump. Pressures were measured by means of a McLeod gauge placed on the high vacuum side of the Langmuir pump. No attempt was made to keep mercury vapor out of the sputtering jars. These were small bell jars provided with leads sealed through the glass, so that the resistance of the films could be measured in situ. Resistances were measured on a Wheatstone Bridge.

The films were sputtered on small strips of glass prepared in a manner similar to that described by Richtmyer and Curtiss,[3] and were about 11 mm. long by 13 mm. wide. The films were deposited at a pressure in the neighborhood of 0.03 mm. of mercury. In order to have fairly constant pressure conditions during deposition a discharge was first passed through the jar for about an hour. During this time the blank was protected by an aluminum shield of the shape shown in Fig. 1, which was mounted on a pivot in a horizontal position. This shield carried several small pieces of iron on its upper surface so that, when the jar was sufficiently freed of occluded gases, it could be swung around from without, by means of a magnet, and the opening placed over the blank. The distance between the blank and the cathode was from 1.5 to 3 cm. The length of the cathode dark space under the conditions of operation was about 1 cm. The necessary voltage was obtained from a transformer operating on the 110 volt circuit and was in the neighborhood of 10,000 volts. In order to avoid excessive heating of the jar and of the film during deposition, an interrupter was placed in the primary of the transformer circuit which opened the circuit for about 5 seconds out of every 6. The stopcocks in the system were

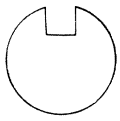

Fig. 1.

[1] Longden, PHYS. REV., 11, 40, 1900.

[2] Hobbs, Phil. Mag., 32, 141, 1916.

[3] PHYS. REV., 15, 465, 1920.

greased with a special grease having a low vapor pressure, prepared as described by Booth.[1]

NORMAL AGING IN VACUO.

If a sputtered film is allowed to age in the air of the laboratory its resistance will decrease rather slowly, and perhaps somewhat irregularly, for a period of many weeks or even months before it settles to a nearly constant value. If the film is allowed to age in vacuo (that is if the

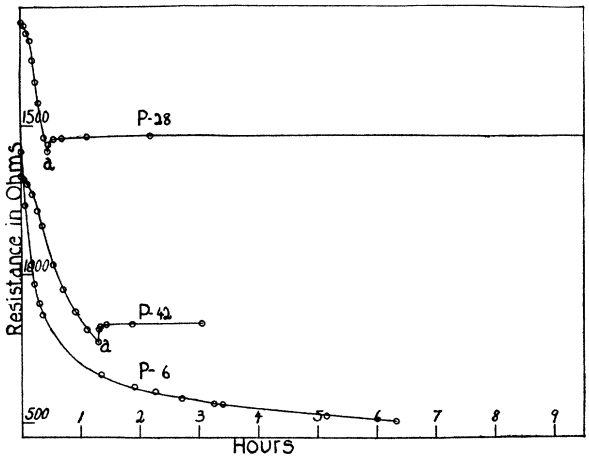

Fig. 2.

pressure is kept below 0.005 mm. by running the pumps) the time resistance curve will be of the form shown by P. 6 Fig. (2). The initial reading here was taken immediately after stopping sputtering, and the pumps were kept running during the entire course of the observations. The initial value of the resistance was about 1,400 ohms and it dropped to a final value of approximately one third of this. This curve is typical in general form for both thicker and thinner films. In all cases the resistance decreases very rapidly at first and then gradually more and more slowly until finally after about 12 hours the rate of decrease is almost negligible. In the case of thinner films the total drop is relatively greater and of thicker ones relatively less for reasons which will be discussed later. The general form of the curve, however, is the same for all films.

Evidently what is taking place here is a process of settling down and of agglomeration, or coalescence or sintering, the last three terms being more or less synonymous. In view of the lack of exact knowledge of the

[1] H. S. Booth, Thesis, Cornell University, 1919.

process coalescence is probably the best term to apply. This process has been studied for many substances both crystalline and amorphous. Bancroft[1] cites the cases of the sintering of tungsten and tantalum powders at temperatures far below the melting point and comes to the general conclusion that "liquid drops or solid grains will coalesce or agglomerate if brought into actual contact." Since we know from the work of Mr. Kahler[2] done in this laboratory that sputtered films are made up of small crystals, it is easy to form a picture of the mechanism by which the resistance is changed. The resistance of a film having this granular structure must consist of two parts; first, a purely metallic resistance, and secondly, a part due to the contacts between the particles. The first part of the resistance is not changed by aging, but the second, namely that due to the contacts, must be diminished, since as the small particles coalesce to form larger ones some of the contacts must disappear. This process, of course, can only result in a lowering of resistance when the film contains sufficient metal so that the coalescence may proceed without actually causing breaks. For this coalescence to take place readily the particles must actually come *into contact*, which can only take place in vacuo.

Effect of Adsorption of Air.

If, instead of allowing the process to run to an end in vacuo, air is admitted to the jar a different result is obtained, as is shown by curves P. 28 and P. 42 in Fig. 2, where air at atmospheric pressure was admitted at the points marked *a*. The result is the same whether air is admitted immediately after sputtering or several hours later. Upon the admission of the air two things take place; first, a slight rise in the resistance of the film, and second, a nearly complete stoppage of the aging. This is due to the fact that each particle becomes surrounded with an adsorbed air film which tends to prevent further contact and coalescence. This prevention of coalescence by an adsorbed air film is merely an illustration of what takes place in every colloidal suspension; namely, the suspended material is kept from precipitating out by an adsorbed film either of a peptizing agent added for this purpose, or by an adsorbed film of the dispersion medium. In this case the disperse phase (platinum) is peptized by an adsorbed film of the dispersion medium (air). The rise in resistance is evidently due to a rearrangement of the little particles, most likely with a widening of the gaps between them as the air film is adsorbed.

[1] Bancroft, Applied Colloid Chemistry, p. 153.

[2] Kahler, PHYS. REV., 17, 230, 1921.

If this theory is correct, since true adsorption is a reversible phenomenon, it ought to be possible to remove the air film by reëvacuating the sputtering jar and then the aging ought to continue. This is shown by curve P. 22 of Fig. 3. Air admitted at the point marked *a* had brought

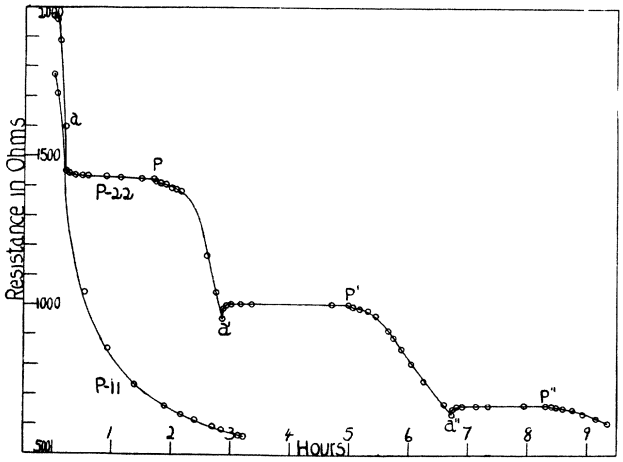

Fig. 3.

the aging to a stop. The pumps were started operating at the point marked *p*. The resistance began to fall, at first gradually and then more rapidly, until it finally reached almost the same rate of fall as before the admission of the air. At *a'* the air was again admitted and the aging stopped, and at *p'* the pumps were started with the same results as before. Similarly at *a''* and *p''*. Curve P. 11 in the figure is plotted for comparison and shows the aging in vacuo of a film having about the same initial resistance. It will be noticed that the final values of the resistance reached are of the same order, and that the corresponding portions of the aging curves are of very much the same form. The only effect of the air has been to halt the aging temporarily without producing any permanent change in the film.

A closer study of some of the portions of the aging curves gives additional evidence of the correctness of this adsorption theory. First of all consider the rise in resistance when air is admitted to the sputtering jar. The greater part of this rise takes place in the first two or three minutes and after that it continues at a gradually decreasing rate for several hours. (This behavior is characteristic of all adsorption phenomena, where the equilibrium is nearly reached in the first few minutes, but is not complete until after a lapse of several hours.) Later a slight gradual fall in resistance may take place. Although the film may continue to

age thus at a slow rate for a long time it shows no signs (over a period of several months) of dropping to the value which it would have reached if it had been aged in vacuo. The time required to reach the maximum depends on the resultant of the rate of aging and the rate of rise due to the gas.

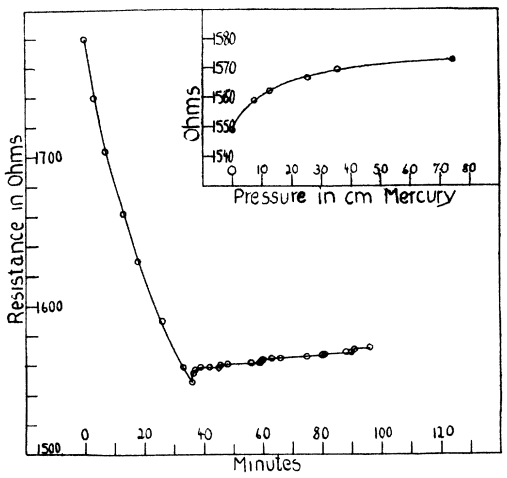

Fig. 4.

If this rise is due to adsorption of gas by the film it should be a function of pressure. This was actually found to be the case as shown in Fig. 4 In this case instead of admitting air at atmospheric pressure at once it was admitted in several instalments, allowing time in each case for equilibrium to be established. According to the theory of adsorption, at each pressure a definite amount of gas must be adsorbed, corresponding to which there is a definite value of the resistance of the film. A further increase in pressure will result in more gas being adsorbed and a further rise in resistance. When the final values of resistance are plotted against pressure a smooth curve is obtained, similar in general form to the adsorption isotherm.

On reversing the process and pumping out the air the exact same curve is not reproduced. The resistance drops slowly with decreasing pressure until in the neighborhood of 0.020 mm., below which it falls off very rapidly. Apparently once the aging has been stopped only a very small amount of adsorbed gas is required to prevent it from continuing, whereas it takes a much larger amount of gas to bring it actually to a stop. This is shown by a closer study of the portions of the curve marked p in Fig. 3. This has been plotted to a larger scale as curve 1 in

Fig. 5. If the values of resistance are plotted against pressure instead of time the result is shown by curve 2 in the same figure. This shows the gradual decrease in resistance till in the neighborhood of 0.020 mm. and the more rapid rate of fall as the pressure falls below this. This also explains the apparent lag observed at the beginning of many of the aging curves. This is not really a time lag of the films, but merely represents the time required for the pumps to bring the pressure from the sputtering value down below the critical value.

The pressure at which the films are sputtered is well above the critical value. This was shown by closing the stopcock leading to the sputtering jar immediately after sputtering, thus keeping the film at the pressure at which it was sputtered. When this is done the aging is very slight and the resistance time curve is nearly flat. As soon, however, as the stopcock is opened and the pumps are started the adsorbed air is given off and the resistance drops very rapidly.

Effect of Adsorption of Gases other than Air.

Some rough qualitative experiments were undertaken to determine the behavior of the films towards gases other than air. Since adsorption is a specific phenomenon the behavior of the films ought to vary with the nature of the gas, which was found to be the case.

One factor which influences the resistance of the films greatly is that the process of sputtering activates the platinum so that both the sputtered film and the cathode from which it was sputtered cause hydrogen and oxygen to combine at room temperature. This reaction takes place very rapidly; both the cathode and the thick deposits on the walls of the jar becoming quite hot, while water vapor is condensed on the cooler parts of the jar. The platinum deposits on the edges of the mica backing of the cathode are heated to incandescence and cause a mixture of hydrogen and oxygen to explode. This property of platinum is well known but so far as the writer is aware this method of activating platinum by sputtering is new. In this connection it would be interesting to study the catalytic properties of other sputtered metals; and also to see whether the substances which are known to poison catalysts have any effect on sputtering, and whether substances which are known to prevent sputtering have any effect on catalysts.

Instead of admitting air to the sputtering jar, as already described, its chief constituents were tried separately. Nitrogen in small quantities (pressure 2–3 cm.) hardly affects the aging appreciably. At a pressure of one atmosphere it slows the aging down very much but does not bring it absolutely to a standstill. Even a small amount of oxygen

is effective in stopping the aging and giving the characteristic rise which has already been described; while increasing the concentration (pressure) of the oxygen gives further rises in resistance. This shows that the active constituent of the air is the oxygen, which is strongly adsorbed, while the nitrogen is only taken up to a much lesser extent.

Carbon dioxide behaves in much the same manner as nitrogen.

If hydrogen is admitted, after oxygen has been admitted and pumped out again, the resistance of the film will drop several hundred ohms almost instantaneously, and will continue to fall at a gradually decreasing rate for some time. This is due to two causes. One is the heat developed by the reaction of the hydrogen with the oxygen previously adsorbed by the film, which accelerates the aging; and the other is due to the removal of the oxygen from the surface of the particles by combination with the hydrogen, which has the same effect as pumping. An increase in the hydrogen pressure will result in a further drop in resistance because the velocity of the reaction between the hydrogen and oxygen is a function of the pressure. Hydrogen has the same effect even if oxygen has not been previously admitted because the film contains oxygen which was adsorbed during the process of sputtering. When the hydrogen oxygen reaction has run to an end the aging is gradually brought nearly to a stop by the adsorption of hydrogen.

If the hydrogen is nearly completely removed by pumping and oxygen is admitted the characteristic rise is observed. This is because the oxygen is much more strongly adsorbed than the hydrogen, and the rise due to the adsorption of oxygen masks the heating effect of the reaction with the very slight amount of hydrogen in the film. If now the oxygen is removed by pumping and hydrogen is readmitted another sudden drop will take place due to the heating when the hydrogen combines with the additional oxygen which has been taken up by the film. Miss Hobbs[1] observed that when a film has been deposited in hydrogen the effect of admitting hydrogen is a rise in resistance, while in the case of a film which has been deposited in air the hydrogen may produce a fall in resistance which seems to substantiate the writer's theory.

Illuminating gas has the same effect as hydrogen (to a slightly lesser extent) probably because it contains a large percentage of hydrogen.

It was found that at times the admission of air caused a sudden drop in resistance instead of the usual rise. This effect is shown at *a* in Fig. 3. This is due to the presence of traces of illuminating gas in the air of the laboratory.

[1] *Loc. cit.*

Temperature Coefficients.

Another very interesting property of sputtered films is that their temperature coefficients of resistance are smaller than the temperature coefficients of the same metal in bulk. Patterson[1] made some measurements of the temperature coefficients of platinum films and found an apparent relation between the temperature coefficient and the thickness. Swann[2] also made measurements of temperature coefficients on the basis of which he formulated a theory of the mechanism of conduction in thin films. According to Swann's theory the films owe their properties to their granular structure and not to their thickness. Longden[3] measured the temperature coefficients of very thin films and found them negative. Thicker films had positive coefficients, and some intermediate films had zero coefficients. Longden attempted to show from

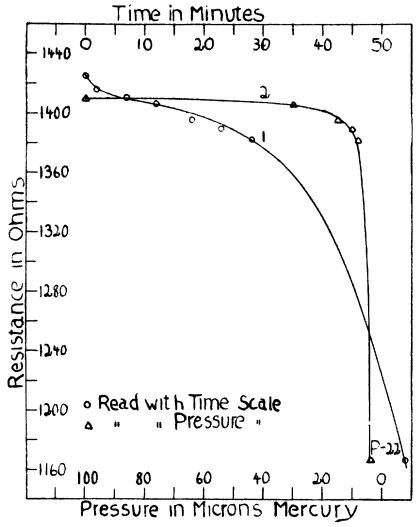

Fig. 5.

his work that there was a linear relation between thickness and temperature coefficient.

In this part of the work the resistances were measured as before on a Wheatstone Bridge. The films were in a test tube placed in an oil bath, which was electrically heated and constantly stirred. Temperatures were read on a thermometer immersed in the oil. The measurements covered the range from room temperature to 200° C.

The first time a film is heated its resistance may show an initial rise

[1] *Loc. cit.*

[2] Swann, Phil. Mag., 28, 467, 1914.

[3] *Loc. cit.*

or it may begin to fall at once, but in all cases on further heating the resistance falls quite rapidly. This initial difference in behavior is probably due to the fact that the films were of different ages and had reached different stages in the aging process. The rapid drop in resistance when plotted against temperature gives a smooth curve which is rather misleading. This change in resistance is really a time effect and since the temperature of the bath is also a function of the time the resistance and temperature seem to be related. While the film is being heated two changes in resistance are taking place simultaneously. One is a small rise due to the temperature coefficient. The other is a large decrease due to the more rapid aging at the higher temperature. The higher the temperature is raised above room temperature the greater does the latter become, and until it has proceeded nearly to an end it completely masks the temperature coefficient effect. Thus with each heating the resistance of the film is permanently lowered. After several

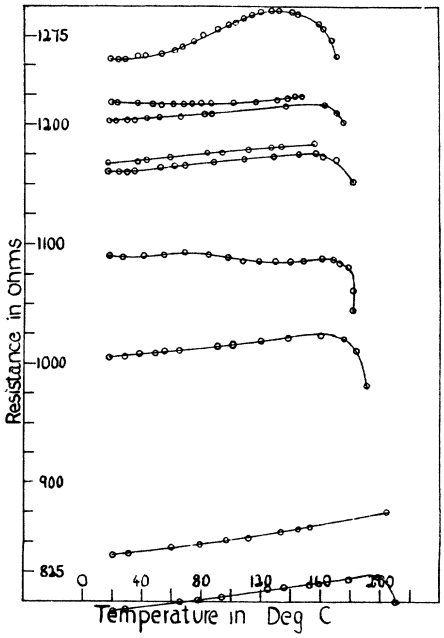

Fig. 6.

such heatings, when the resistance has nearly reached its minimum value the temperature coefficient becomes perceptible, and the heating and cooling curves become nearly straight lines and can be duplicated, provided the temperature is kept well below the maximum temperature of the previous run. Such a series of curves is shown in Fig. 6.

As the initial resistance of the film becomes lower with each run the temperature coefficient becomes greater but the slope of the lines changes very little. This agrees well with the suggestion made before as to the mechanism of aging; the effect of heating is to increase the resistance of the metallic portion of the film due to the true temperature coefficient effect, and to decrease the resistance of the contacts due to eliminating many of them as the particles coalesce. Until the film is well aged the latter effect is by far the greater. As long as the temperature of a film is kept below a higher temperature to which it has previously been raised the aging is small and so the chief change is in the true metallic resistance, and this rise must remain nearly the same for all stages of the aging.

The temperature coefficient then becomes a function of the degree of aging which in turn depends on the temperature to which a film has been heated. If, for example, a film is placed in the oil bath at a temperature of 100° the resistance will fall rapidly at first but after some hours will settle to a nearly constant value. The film will now be quite permanent for all temperatures below 100° and the temperature resistance curve will be nearly a straight line, as long as the temperature is kept below this value. On heating to say 200° aging proceeds further with a still further lowering in the resistance of the film until it finally reaches a constant value again. Again after this treatment the temperature resistance curve will be a straight line, while the temperature coefficient will have been nearly doubled. Patterson assumed that his films were

TABLE I.

Film No.	Initial Resistance.	Temperature Coefficient.	Patterson's Temp. Coef.
85	1570	.000888	.00011 to .00033 approx.
77	1444	.000644	
72	1974	.00108	
58	1866	.00075	
73	506	.00108	
70	93	.00144	.0005 approx.
55	65	.00200	

completely aged by heating them for 60 hours at 100°, but the present work shows that heating to still higher temperature would have reduced the resistance still more and multiplied his temperature coefficients by as much as 4. After aging at the highest obtainable temperature of the oil bath (210°) the films were heated in an oven of which the temperature was estimated to be 500° C. This resulted in a still further lowering

of the resistance and raising of the temperature coefficient. In some cases the resistance became infinite due to the destruction of the gold platinum contact. In such cases a new pair of gold terminals was sputtered overlapping the old ones. This merely changed the effective length of the film. Table I. gives the initial resistances and the maximum values of the temperature coefficients obtained for some of the films, and for comparison the values for films of the same thickness obtained by Patterson. Very thin films were found to have negative temperature coefficients.

The aging due to heating even if done in air is very much greater than that due to a vacuum. The effect of heat is to accelerate the rate of aging, and furthermore heat will reduce the resistance far below the minimum value reached in vacuo at room temperature. For example, a film which had dropped to 376 ohms when aged in vacuo was heated for several hours at 110° and finally reached a value of 316 ohms. On further heating at 200° the resistance dropped to 192 ohms.

On prolonged heating at the higher temperatures the resistance of all except the very thickest films passes through a minimum, becoming very large and finally infinite. This point of minimum resistance is reached at lower temperatures the thinner the films. The explanation given by Kohlschütter and Noll for a similar phenomenon in the case of silver films probably holds good here, namely that as the coalescence proceeds it finally reaches a point where there is not sufficient metal in the film for it to take place without rupturing the film. In this condition the films must be very much like the extremely thin films in which Swann describes the distribution of particles as being similar to the condition of affairs on a pavement when rain drops begin to fall, and before enough drops have fallen to cover the pavement. The difference probably is that in the case of films which have been brought to this state by excessive heat treatment the individual particles must be larger. Since the very thin films have negative temperature coefficients it would be expected that these high resistance thick films would also have negative coefficients. These films, however, are in such an unstable condition that it is extremely difficult to make measurements with any degree of certainty. One such film was found to have a negative coefficient, but although several other films were studied this could not be confirmed.

A study of Table I. will show that the thickest films have the largest temperature coefficients and that the values decrease as the films become thinner. The maximum value is about four sevenths of the value of that for platinum in bulk. These values are higher than the ones obtained by Patterson because the aging was carried on at higher temperatures and therefore proceeded further. The fact that the tempera-

ture coefficients increase with increasing thickness is probably not due to the thickness or thinness of the film, but to the fact that the thinner films could not be aged to the same point as the thicker ones without destroying them. In other words the temperature coefficient of a film depends not on its thickness but upon its degree of agglomeration. Probably all films have the same temperature coefficients when aged to the same point.

Films deposited on quartz were found to have the same temperature coefficients as similarly treated films of the same thickness on glass.

In the table the initial resistances of the films are given, but as a matter of fact a serious error would be introduced if the thickness of films was to be determined on the basis of a comparison of initial resistances. A film having a resistance of the order of 10^6 ohms will fall on heating to 10^3 ohms, while one having an initial resistance of 1,000 ohms will fall under the same conditions to 100 ohms. The ratio of the final conductances of these two films, which is about the same as the ratio of the times of sputtering, gives a true idea of the amount of metal in them; while the ratio of the initial conductances would be entirely misleading. The reason for this is that the films age during the process of sputtering, probably partly due to the impact of the particles and mainly due to the heating. Thus a thicker film, which during the course of sputtering has been exposed to more heating has therefore aged more and so for the same amount of metal has a lower resistance.

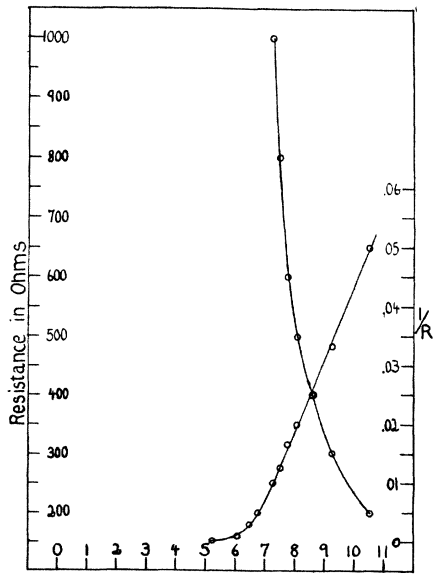

Fig. 7.

The aging due to the heat of sputtering was tested as follows. A film was sputtered in the usual way and the aging stopped by admitting air. A thin microscope cover glass was then placed directly on top of the film and the jar reëvacuated. At a pressure well above that at which aging takes place a film was sputtered on this cover glass. This resulted in a rapid drop in resistance which can only be explained by the heating effect of the sputtering.

In order to obtain some more information in regard to what takes place during sputtering measurements of resistance were made while sputtering and plotted against time as shown in Fig. 7. The reciprocals of these resistances when plotted against time give a straight line excepting during the very early stages of the deposition. If the conductivity increased by equal increments in equal times this curve should pass through the origin. The fact that it does not do so indicates that during sputtering in addition to depositing more metal the resistance of the metal already deposited is also growing less, thus giving the line a steeper slope than would be due to deposition of metal alone.

According to the theory of J. J. Thomson there should be a rapid increase in resistance below a certain critical thickness; this critical point being that at which the dimensions of the film become comparable with the mean free path of an electron. Patterson's results seem to show that the specific resistance of the films increases very rapidly with decreasing thickness below a thickness of 7×10^{-7} cm. which is in accordance with the theory. From this bend in the specific resistance thickness curve Patterson computes the mean free path of an electron. It is extremely doubtful whether the Thomson theory can be applied directly to sputtered films, the thickness of which is an indefinite quantity. In some places where the groups of crystals are piled up the thickness may be comparatively great while in others it may be very much less. While the specific resistance undoubtedly depends on the thickness the conditions in the film are such that the thickness is not uniform, and the Thomson theory which has been developed for uniform films does not necessarily apply here. The *physical condition* of the film is probably a much more important factor than the thickness.

Patterson's films were all aged at a temperature of 110°. Heating to a higher temperature would have lowered the resistance of all of them, but very likely not in the same ratio, and the thicker ones would probably have been lowered more than the thinner ones, so that possibly the shape of Patterson's specific resistance thickness curve would be altered.

Swann treats the films as "groups of molecules not pressed into intimate contact so that it is only those electrons which have more than a certain minimum velocity, depending on the closeness of packing, which

can travel from one group to the next. This necessary velocity gets less as the time of deposit increases and the groups are pressed more intimately into contact by the greater molecular forces brought into play." This theory seems in accordance with the facts observed in the present work. The numerical values of Swann, however, are open to the same criticism as those of Patterson, namely that the films were insufficiently aged.

In conclusion the writer wishes to express his thanks to Professor Richtmyer who suggested the problem and whose enthusiasm and encouragement made the work possible.

CORNELL UNIVERSITY, ITHACA, N. Y.