RESISTIVITY AND RECOMBINATIONS IN EXTREMELY THIN METALLIC LAYERS

Thesis by

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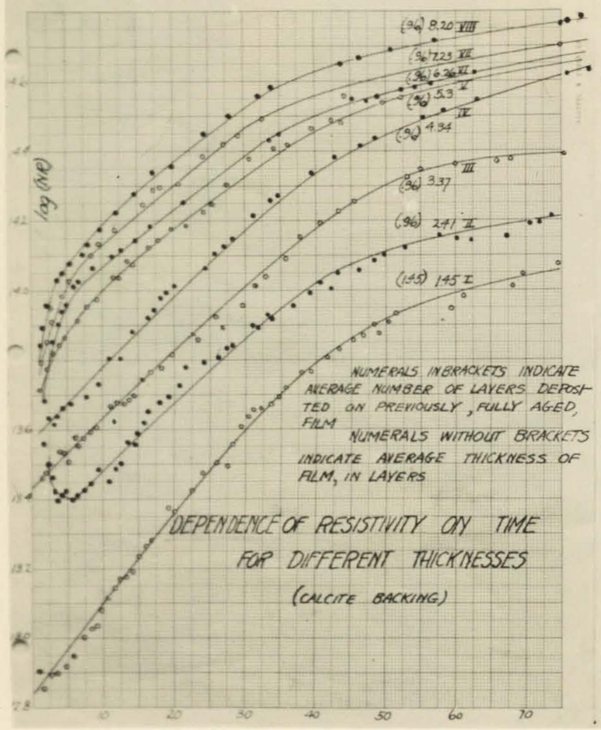


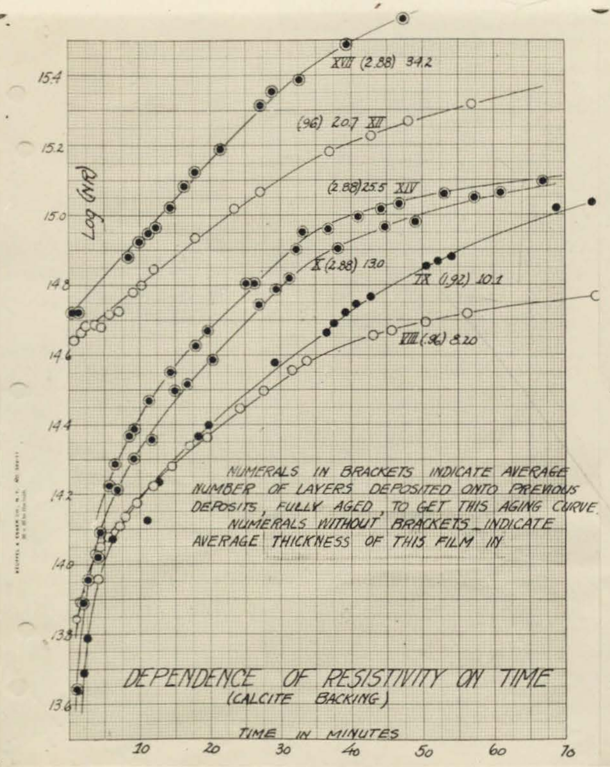
NUMERALS IN BRACKETS INDICATE AVERAGE NUMBER OF LAYERS DEPOSITED ON PREVIOUSLY, FULLY AGED, FILM

NUMERALS WITHOUT BRACKETS INDICATE AVERAGE THICKNESS OF FILM, IN LAYERS

DEPENDENCE OF RESISTIVITY ON TIME FOR DIFFERENT THICKNESSES

(CALCITE BACKING)

FIG. 19

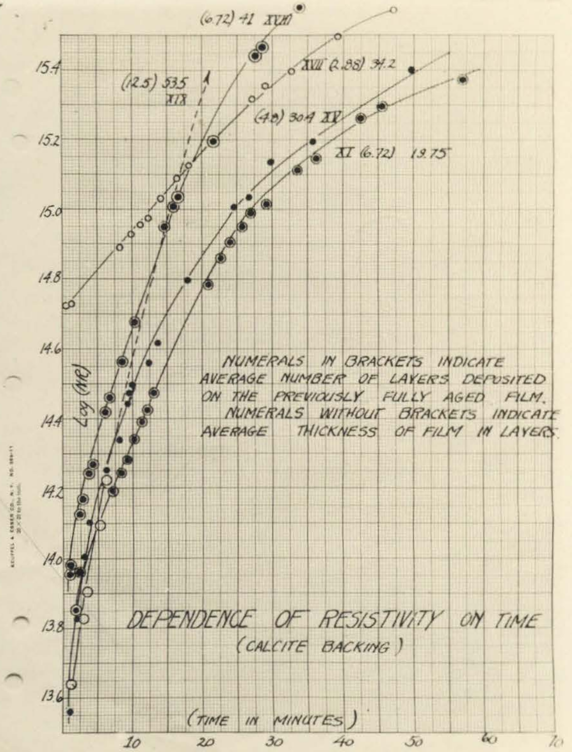


NUMERALS IN BRACKETS INDICATE AVERAGE NUMBER OF LAYERS DEPOSITED ONTO PREVIOUS DEPOSITS, FULLY AGED, TO GET THIS AGING CURVE. NUMERALS WITHOUT BRACKETS INDICATE AVERAGE THICKNESS OF THIS FILM IN

DEPENDENCE OF RESISTIVITY ON TIME

(CALCITE BACKING)

FIG. 20



NUMERALS IN BRACKETS INDICATE AVERAGE NUMBER OF LAYERS DEPOSITED ON THE PREVIOUSLY FULLY AGED FILM. NUMERALS WITHOUT BRACKETS INDICATE AVERAGE THICKNESS OF FILM IN LAYERS.

DEPENDENCE OF RESISTIVITY ON TIME

(CALCITE BACKING)

FIG. 21

I. Introduction.

Thin metallic films show many strange and peculiar properties that differ considerably from those exhibited by a massive chunk of the same metal. These properties have been the object of much investigation in the past and may be briefly summarized:

(1) The specific resistance remains constant with decrease of thickness down to a certain value, often called the critical thickness, at which point it suddenly jumps towards infinity.

(2) This critical thickness is variously estimated in the neighborhood of 70×10^{-8} cm. It seems to depend upon a number of variables: the kind of metal; the experimental conditions; and the way the measurements are made.

(3) All films show irreversible changes of resistance with temperature; with the passage of heavy current; and with time.

(4) The presence of a gas affects the properties and structure of the film.

(5) The crystal structure of the film is determined by the mean film thickness; the type of backing; and the temperature at which the film is formed.

As the above five points - unlike the following one - will be discussed more fully later, references are omitted.

(6) Finally the thermoelectric power(1); the change of resistance in a magnetic field - Hall effect(2...18); and the photoelectrical and optical properties - for which Schulze(19) gives a

most complete bibliography including about 70 workers - show peculiarities.

As the major interest in this article will be centered about the resistance properties of thin films, particularly those depending on thickness and aging, previous results for these will be analysed and discussed more in detail. The best method of approach is from the standpoint of the critical thickness, since most investigators give their resistances in arbitrary units which are impossible to evaluate; and, as will be seen, aging runs hand in hand with the critical thickness.

In the following is given a tabulated historical summary of the critical thickness as a function of the kind of metal, the method of producing the film, together with the name of the investigator and the year in which he obtained the results.

Numbers in ( ) indicate reference in bibliography
C.T. denotes critical thickness in mμ

Metal	Wet process	Sputtering	Evaporation
(Ni)	Moreau (4), 1901, deposited Ni on Ag mirrors. C.T. = 24.	Reide (10), 1914, C.T. = 3 (11), 1918, C.T. = 1.25 (11), 1924, C.T. = 3.0 All these were sputtered in H_2. All curves show peculiarities which are probably due to a metal hydride.	

(Ca)		Reide (10), 1914, C.T. = 2.8 Deposited as above	Steinberg (48), 1923, C.T. = 12. Only the backing was outgased. The walls and tube were of brass.
(Pd)		Pogony (46), 1916, C.T. = 25.	
(Pt)		(1) Patterson (45), 1902 C.T. = 4. (2) Reide (10), 1914, C.T. = 1.2 (3) Reide (11), 1928, C.T. = 2 to 3. (4) King (6), 1917, C.T. ≑ 1.5 to 3. (5) Pogony (46), 1916, C.T. = 1. (6) Joliot (33), 1928, C.T. = 2.5 (7) Fery (49), 1928, C.T. = 3 (8) Perucca (50), 1930, Finds that C.T. is 4 times that of gold under similar conditions	Weber and Oosterhuis (47), 1917, C.T. = 12 which agreed with 2 other trials made. Tube was baked out and the measurements made at 32°C. He also compared the conductivity of films of different metals at the same temperature: (Ag) begins to conduct at 2 x 10^8 ohms at a thickness of 12 molecules. At this point (Pt) has a resistance of only 300 ohms and is 2 to 3 molecules thick. And tungsten has a resistance of 150 ohms and is 1 atomic layer thick.
(Au)		King (6), 1917, C.T. = 6 to 8. MacKeown (2), 1924 C.T. = 3.2 Perucca (50), 1931. Finds that film conducts at ($\frac{1}{4}$) the thickness of Pt.	Hamburger (35), 1931, C.T. = 3.
(Ag)	Vincent (3), 1900, C.T.= 50. Reide (10), 1914, C.T.= 35. Wait (5), 1922, C.T.= 20.	Patterson (45), 1902 C.T. = 5. King (6), 1917, C.T.=6to8 Pogony (46), 1916, C.T. = 4.5.	Weber and Oosterhuis (47), 1917, C.T. = 6.5. Steinberg (48), 1923, C.T. = 25.

(Hg)		Volmer and Estermann (51), 1930, C.T. = 200. Evaporated from a pool of mercury and condensed on glass at liquid air temperature.
(W)		Braunsfurth (51), 1930, C.T. = .8 Weber and Oosterhuis (47), 1917, C.T. = .43 Hamburger (35), 1931, C.T. = .2
Rh	Braunsfurth (23), 1930, C.T. = 6.	
Ir-Rh	Braunsfurth (23), 1930, C.T. = 2.2	

The table shows a great lack of agreement among the various investigators on the critical thickness, even when they use the same method in producing the film. This, I believe, can be accounted for on the basis that not sufficient consideration was given to the following facts:

(A) Occluded gases modify considerably the properties and structure of thin films:

E. W. Hobbs(20) and W. Reynolds(21)(22) find that gas in the presence of a film causes the film to decrease its resistance with time. And if the gas is pumped off, the resistance increases slightly with time. Braunsfurth(23), Ingersoll and Hanawalt(24) confirm this, and in addition show that great amounts of gas are absorbed in the process of sputtering.

The presence of gas has often been shown to cause changes of crystal structure and lattice constant together with the formation of compounds. G. P. Thomson(25) finds that (Ni) which is normally cubic, when sputtered in (Ar), on rocksalt is hexagonal; Ingersoll and Hanawalt(24) find that (Ni) sputtered in (N_2) or (H_2) has a different structure from parent metal, and also that (Fe) and (Co) sputtered in (He) suffers an increase of lattice constant as much as 20%. Other investigators: Lauch(27), Kohlschutter and Noll(28) and Allolio and Bredig(29) obtain like results which tend to the conclusion that the presence of foreign gases, during or after the formation of the film, may produce hopelessly complicated experimental conditions.

From these facts it may be concluded that experimental results gotten from films produced by the wet process or by sputtering, are open to grave criticism, as foreign atoms are always unavoidably present at a considerable density.

(B) The sputtering process forms the film from small particles of the metal rather than from individual atoms:

V. Kohlschutter(30) and Houllevigue(31) as a result of their investigations show that a metal, when sputtered, comes down in chunks; and the size of these depends on the gas present during sputtering.

(C) Properties of a film are very sensitive to temperature changes which may cause irreversible changes in film:

Braunsfurth(23) has shown that these films decrease their resistance with temperature, whereas, the resistance of thicker ones increases with temperature. Also a film may take on any value for the temperature coefficient of resistance from zero to a maximum value, depending on its degree of aging. Furthermore, an hysterisis effect makes its appearance. This is evidenced by the fact that the curve representing resistance as a function of temperature always lies higher when the film is being cooled than when being heated. This is an irreversible effect and seems to be more pronounced as the quality of the vacuum improves.

Like results are secured by W. Reynolds(21), Bartlet(32), Hamburger(35), and M. F. Joliot(33) who in addition show that a film will show reproducible properties at all temperatures below the maximum to which it has previously been subjected, but irreversible above this.

Horowitz(36) and Homburger show that films deposited at liquid air temperatures have no crystal structure, whereas, those deposited at room temperature do.

Ingersoll and Sordahl(34) point out that a temperature rise, always accompanying sputtering, produces a considerable change in the resistance properties of the film.

The above facts lead to the conclusion that definite precautions must be made at all times to maintain the constancy of the temperature, when the effect of some other variable is being investigated. In the table, with the exception of Volmer and Estermann, and Weber and Oosterhuis none of the investigators mention that any such precautions were made.

(D) Films undergo spontaneous irreversible changes in structure and properties; often called aging:

Hobbs(37) and Braunsfurth(23) find that films, immediately after their formation by sputtering, show a decrease of resistance with time. The same result is shown more clearly by Bartlett(32) and Koller(38) who account for the decrease on the basis of the coalescence and crystallization of the metallic particles.

These facts indicate that film-resistance depends considerably on film-aging. None of the workers mentioned in the table - as far as I have been able to determine - allow any time for aging while taking their measurements.

(E) The measured film-properties depend on the backing:

S. Dembinska(39), producing her films by evaporation, and observing their structure from x-ray diffraction patterns decides that different types of film-backing produce different uniformities of film structure. She deposits gold films onto: an aluminum single crystal; mica; glass; and quartz, and finds that the sharpness of the x-ray diffraction patterns increase in the same order. The lattice constant she finds, however, remains the same as for the parent metal.

The results of F. Kirchner(40) make the above conclusion rather doubtful and seem to indicate that uniformity of film-structure is determined principally by film-thickness. Results obtained from evaporated films and by using electron diffraction, show that - when both celluloid and mica are used as backing - initially the film is colloidal; then with increase of thickness some crystallographic axis of the small nacent crystallites lines itself parallel to the backing; later, a crystallographic plane lines itself up parallel to the backing; and finally there is a complete allignment of all the small crystallites into a single-crystal.

The difference in coefficient of expansion between the film and the backing may cause strange and misleading effects: A metallic film deposited at room temperature on quartz and then cooled down to that of liquid air is placed under an increasing amount of tension, and might even finally be ruptured. This is because of the difference between the coefficient of expansion for quartz and the metallic film. Bartlett(32) finds that identical films, normally with large positive temperature coefficients of resistance, when deposited on different backings do not show the same temperature coefficient of resistance; he finds that the smaller temperature coefficient of expansion of the backing, the smaller the temperature coefficient of resistance.

Any tension or compression of the film should always be relieved before the film-properties are investigated. This can be accomplished by annealing the film or, prefferably, the film should be deposited at the same temperature at which its properties are to be determined.

(F) The methods employed in the past for determining the thickness of extremely thin films are not all that is to be desired. Either they are not sufficiently sensitive, or they preclude the possibility of keeping the film in a high vacuum.

They may be divided into the following broad divisions:

(1) Optical Method: (a) Interference, (b) Opacity.

(2) Electrolysis.

(3) Mechanical Method.

(1a) Quinke(41), Fizeau(42), Wernike(43) and Wiener(44) have developed methods for determining film-thickness from the interference colors. This method however is not applicable to films much thinner than the wavelength of visible light. Furthermore, each determination is extremely laborious and must be made in air outside of the apparatus, with the contamination of the film as a consequence.

(1b) MacKeown(2) and others have shown that there exists a linear relation between film-opacity and film-thickness. This forms the basis of a method for determining film-thickness. What is done is to measure the opacity of a few thick films whose thickness can be determined by weighing. From these, the straight line relation is found. The thickness of other films are now gotten merely by measuring their opacity and extrapolating on the curve.

This method is likewise not adapted for extremely thin films; both because the opacity becomes imperceptible and because thin films undergo spontaneous changes in structure with time, which change their optical properties.

(2) Schulze(19) describes a method for transforming thick films of known thickness into thin ones, also of known thickness, by electrolysis. The thick film, whose thickness may be determined by weighing, is placed in an electrolytic cell; and through it is passed a known current for a known time. Then applying Faraday's Law, the number of atoms removed from the film is easily calculated.

This method suffers from two serious objections: The film is contaminated by foreign atoms, and the resulting film is quite non-uniform in thickness.

(3) The mechanical method is the most prevalent. It presupposes the constancy of the rate of deposition, which may be determined by depositing a thick film for a known time and weighing it. The thickness of any other film, deposited at the same rate, is then merely the product of this rate and the total time of deposition.

Thickness determinations in the past, by this method, have been far from satisfactory in my opinion. Those carried out by sputtering are open to the usual criticism; those by evaporation because no adequate precautions were taken to ensure a uniform rate of evaporation. Take Oosterhuis' work as an example. He electrolysis a known amount of metal onto a tungsten filament;

and then by heating the filament up, evaporates this metal. He has no arrangement, such as a thermocouple, on the filament enabling him to determine its temperature. He must rely either on an optical pyrometer or the maintainance of the constancy of the current through the filament. With the exception of the furnace described by Goetz(52), none in the past - in the author's opinion - ~~are~~ is capable of evaporating at a uniform rate.

The other properties of thin films have not been investigated as thoroughly as conductivity. On the other hand, the quantitative agreement on them is found to be somewhat better. However, as they will be of no immediate interest in what follows, they will not be discussed at present.

(II) Conclusions from a Consideration of Previous Work.

Out of the above discussion and criticism of the sources of error inherent in the experimental methods of previous workers it seems to follow: If any further progress is to be made in research on the properties of extremely thin films, then improved apparatus and technique must be developed.

Towards the accomplishment of this, work was started a little more than two years ago.

Preliminary runs with this apparatus brought out an aging effect of thin films never by anyone before recorded. It was found, immediately following the formation of the film, that the film would begin to increase its resistance; and within an half an hour or more would attain a value several hundred-fold its initial value. All films were found to exhibit this phenomena, whether they were 1 or 300 atoms thick. Previous investigators invariably find a decrease of resistance with time.

The explanation for this disagreement was discovered quite by accident: One of the films exhibiting an increase of resistance with time was left overnight in the apparatus. The diffusion pump was turned off, but the forevac was kept on. In the morning the diffusion pump was again started and the apparatus thoroughly re-evacuated. Another film was deposited over the old layer. I then got the decrease of resistance with time, invariably found by all others. The explanation is then: previous workers made inadequate precautions for eliminating foreign atoms.

A number of attempts at studying resistance as a function of thickness convinced us that aging, far more than film-thickness, determined film-resistance. From this fact and the previous discussion one sees that aging is a most fundamental property of thin films. All other properties seem to depend upon it.

III. Purpose of this Investigation.

The purpose of this investigation was to determine the dependence of aging on (1) time; (2) film-thickness; (3) and type of backing.

The metal used was silver; and the backings glass and calcite; one, an amorphous surface; the other, crystalline.

In the following will be included a description of the apparatus evolved for producing the films; for measuring their conductivity; and for measuring film-thickness, of monomolecular dimensions, within an accuracy of 3% or better. A theory will be proposed leading to two formulae which satisfactorily describe the aging effect - the trend of resistance with time. One applies to extremely thin films and is $\text{Log } R = kt + c$, where (R) is the resistance; (t) is time; (c) is a constant of integration; and (k) is a constant which, as will be later shown, is the coefficient of recombination of atoms on the surface. The other formula applies to thicker films from a film-thickness of 30 to 40 and up to at least 370 atomic layers. It is: $R = kt + c$, where (k) is here also a constant.

In addition there will be shown the dependence of the coefficient of recombination (k) on the film-thickness and also on the number of uncombined free atoms which are thrown onto the backing at one time. And furthermore, differing radically from the results of more than a dozen other workers, there will be shown a new dependence of resistivity on thickness in which resistivity begins to drop abruptly at a film-thickness within the same order of magnitude as the size of the "Zwicky Block" and, finally, observations tending to the conclusion, contrary to a previous statement by Perucca(50), that thin films do not obey Ohm's Law.

IV Past Theories of the Abnormal Behavior of Resistance as a Function of Thickness.

Three distinct theories have been proposed in the past:

(A) J. J. Thomson Theory: This explains the rapid increase of resistivity with decrease of film-thickness on the basis of the shortening of the mean free path of the electron, in the direction perpendicular to the film. This theory would probably be satisfactory if the film-structure were the same as it is in the bulk metal; and not, as is found, a great number of atomic patches fitted together into a lace-like structure. Also, it is not satisfactory because it does not explain the sudden change of resistivity with thickness, as it is found; and also because it gives a wrong prediction for the change of the critical thickness with temperature.

Recently Tisza(53), on the basis of the Sommerfeld theory, and the shortening of the mean free path of the electron perpendicular to the film - as in Thomson's theory - has predicted a critical thickness. However, he merely gives the final formula without details; and gives no experimental evidence to quantitatively support it. It should likewise suffer from the same objections as Thomson's theory.

(B) Non-conducting Layer Theory: This is the most recent and was advanced by Perucca(50). From experimental data he arrives at the conclusion that the surface layers of all metals are non-conducting and hence possess no free electrons. Whenever the film-thickness is less than twice this hypothetical value the film shows no conductivity.

Such an hypothesis is untenable, as shown by Weber and Oosterhius(47), and Homburger and Reinders(35). They show that films with a mean thickness of even one atomic layer show conductivity. The reason for the disagreement is probably that Perucca formed his films by sputtering; whereas the others, by evaporation.

(C) Granular Theory: This was proposed and given the most thorough theoretical treatment by Swan(54). Other supporters of it have been Houllevigue(31), King(6), Reide(11) and MacKeown(2).

It assumes that atoms fall on the backing at random, much like raindrops fall on the pavement. In time, due to the mutual atomic forces the atoms condense into small isolated nuclei. These nuclei continue to grow as more atoms rain on the surface; and, finally, with increase of size, they begin to make contact. At this point the resistivity drops sharply, but never attains the value found for the bulk metal. This is because the film is still porous - a remnant of its granular structure.

The granular hypothesis as stated above has gained wide credance although Swan's deductions from it have had little success.

V Hypotheses and Formulae Proposed, Accounting for New Aging Effect.

No hypotheses or formulae have been proposed in the past to account for the new aging effect, as far as I know. This is probably because the new effect has been observed now, only for the first time. It will be shown in what follows that the effect can be accounted for on the basis of the following three premises: (1) The granular hypothesis (2) the influence of the high resistant backing and (3) that atoms exert mutual forces of attraction.

As these formulae will be used subsequently in the interpretation and evaluation of the experimental results, their derivation will be given in detail.

(A) For Extremely Thin Films where the Atoms Cover a Relatively Small Portion of the Backing.

Assume that the atoms fall quite at random on the backing, and initially are arranged much as raindrops on a pavement. Immediately, because of the mutual forces of attraction, a process of coalescence of the atoms sets in, entailing a continuous decrease of the number of isolated particles on the surface.

Now, assume that the mechanism of conduction is the motion of the electrons between these particles. One would therefore expect, if there are (n) free particles on the surface, that the removal of one free particle by coalescence with another would cause a $(\frac{1}{n})$-fold decrease of resistance. This means that (R), the resistance, is inversely proportional to (n):

$$Rn = \text{constant}$$

Now let k = the recombination coefficient of the particles and

t = the time allowed for recombination

Then the fractional decrease of the number of free particles on the surface due to spontaneous recombination is:

$$\frac{dn}{n} = -k\,dt$$

Integrating $\log n = -kt + c$. Now $R\overset{n}{u}$ = constant;

Therefore $\log R = kt + c$.

Experimental results later given show that this formula holds remarkably well up to at least an average thickness of 20 layers.

(k) is, at the same time, both the coefficient of recombination of the particles on the surface and the slope of the curve: log R equals a function of (t).

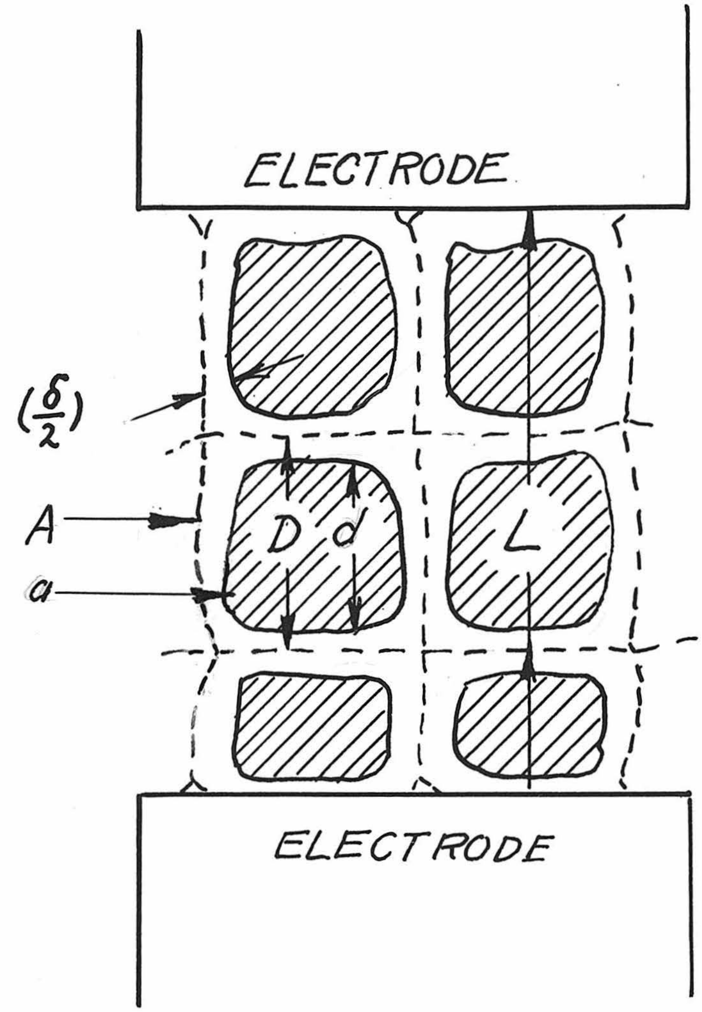
(B) For Thin Films, where the Atoms Cover a Relatively Large Portion of the Backing.

This case differs from the preceding in that the small nuclei have now grown into relatively large patches separated by narrow channels of backing. This enables one to express the total resistance of the film as the sum of two quantities: (1) The resistance of that part of the line of current flow which traverses the channels, i.e., the backing, and (2) of that part which passes through the metallic patches.

Using the symbols as given in the diagram, an expression will be first found for $(\frac{\delta}{D})$ - the fractional part of the line of flow which traverses the backing in terms of the areas of the patches. Letting (A) be the inner plus the outer area, and (D) proportional to its linear dimensions; (a) the inner area, and (d) proportional to its linear dimensions

From geometry: $\frac{a}{A} = \frac{d^2}{D^2}$. Then $\frac{a - A}{A} = \frac{d^2 - D^2}{D^2}$.

PATCH STRUCTURE OF THIN FILMS



(1) (a) is the area of a typical patch

(2) (A) is (a) + (the associated uncovered portion of the backing).

(3) (d) is proportional to the dimensions of (a)

(4). (D) is proportional to the dimensions of (A)

(5) (δ) is (D−d)

(6) (L) denotes a line of current flow.

Fig 1

As $(d - D) \ll D$: $\frac{a - A}{A} = \frac{(d - D)(d + D)}{D^2} = \frac{2(d - D)}{D} = -\frac{2\delta}{D}$.

since $(d - D) = -\delta$ by definition. Therefore $(\frac{\delta}{D}) = \frac{A - a}{2A}$.

Now let (ρ_F) = the resistance of unit length of a solid film and (ρ_B) = the resistance of unit length of clean backing. Then the part of the resistance contributed by the backing is $\frac{\rho_B}{2}(\frac{A - a}{A})$; and by the patches is $\rho_M\sqrt{\frac{a}{A}}$, since $\frac{d^2}{D^2} = \frac{a}{A}$. The total resistance of the film is the sum of these:

$$R = \rho_B \, \frac{1}{2} \, (\frac{A - a}{A}) + \rho_M \sqrt{\frac{a}{A}}$$

Since the patches undergo a coalescence with time, (a) changes. The rate of change of the resistance (R) is consequently:

$$\frac{dR}{dt} = \frac{\rho_B}{A} \, \frac{1}{2}(- \frac{da}{dt}) + \rho_M \frac{1}{2\sqrt{aA}} \, \frac{da}{dt}$$

Since $a \approx A$: $\frac{dR}{dt} = - \frac{\rho_B}{2A} \, (\frac{da}{dt}) + \frac{\rho_{\cancel{B}}^{M}}{2A}(\frac{da}{dt}) = \frac{1}{2A} \, (\frac{da}{dt}) \, (\rho_M - \rho_B)$

Let $A = 1$. This means that we confine our attention to a unit area of the film. Assume now that $(\frac{da}{dt})$ - (the rate of contraction in area of the patches) - is a constant. Later experimental results will justify this. Therefore integrating with respect to time:

$$R = \left\{ \frac{1}{2}(\frac{da}{dt}) (\rho_M - \rho_B) \right\} \times t + c$$

Or $R = kt + c$ where (k) is the expression in brackets.

In verifying this equation log(R) is plotted against log(t), and the curve is always found to be a 45° line.

VI Apparatus

(A) General

In the past, films have usually been produced by sputtering. As pointed out in the introduction this method is open to grave criticism because: (1) the unavoidable presence of gases causes many strange effects and may completely mask the property one is studying, (2) unlike the process of evaporation, where the film is formed from individual atoms, sputtering forms the films from small crystalline chunks or grains pulled out of the cathode, (3) the constancy of the temperature - an extremely important variable - is hard to maintain during sputtering.

On the other hand, the method of evaporation has not been so widely used in the past, although it is open to none of the above criticisms. This is probably because until just recently the technique has not passed far beyond the primitive stage. It is this method we have adopted however; and as will later be shown it presents an admirable means for determining film-thickness with an extraordinarily high precision.

In what follows will be given a description of the apparatus used in depositing the films and for measuring their thickness and their conductivity.

(B) Chamber

(1) General Arrangement of the Parts.

An idea of this can be best gotten by referring to figure 2: (m) is the electrostatic shielding surrounding the chamber;

(F) the furnace support; (e) the crystal holder; (M) the shutter; (u) its magnetic control; and (n) and (r) the water leads for cooling the crystal.

The metal was evaporated from the furnace supported at (F) and condensed on the backing at the lower end of the tube (e). The stream of atoms was colummated by two slits: one at (S) and another at (g). Time exposure was regulated by means of the shutter (M) supported on (W). This shutter was controlled magnetically from the outside by (u).

Potential leads to the film were carried in through two long narrow capillaries (y) - only one is here shown, as the other is directly behind it - and connected to the rods (d) leading to the clamps (g).

An auxilliary furnace, inside the upper end of (W), is required for depositing electrical connections between clamps (g) and the backing.

These connections consisted of relatively heavy films bridging the clamps (g) and the backing, as shown in Fig. 4.

Dependable electrical connection with an adsorbed film can not be made merely by pressing electrodes against the film; the electrodes must be welded to the film, as it were. The reason for using an auxilliary furnace

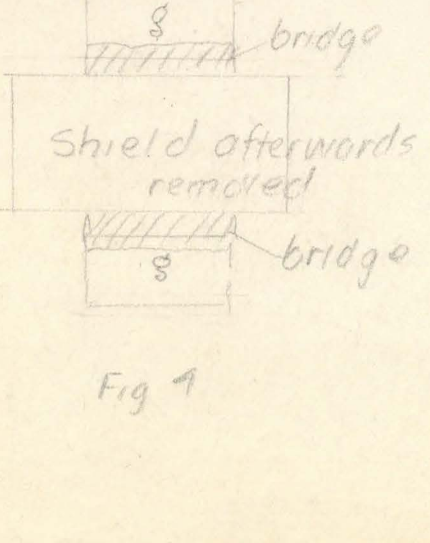


Fig 4

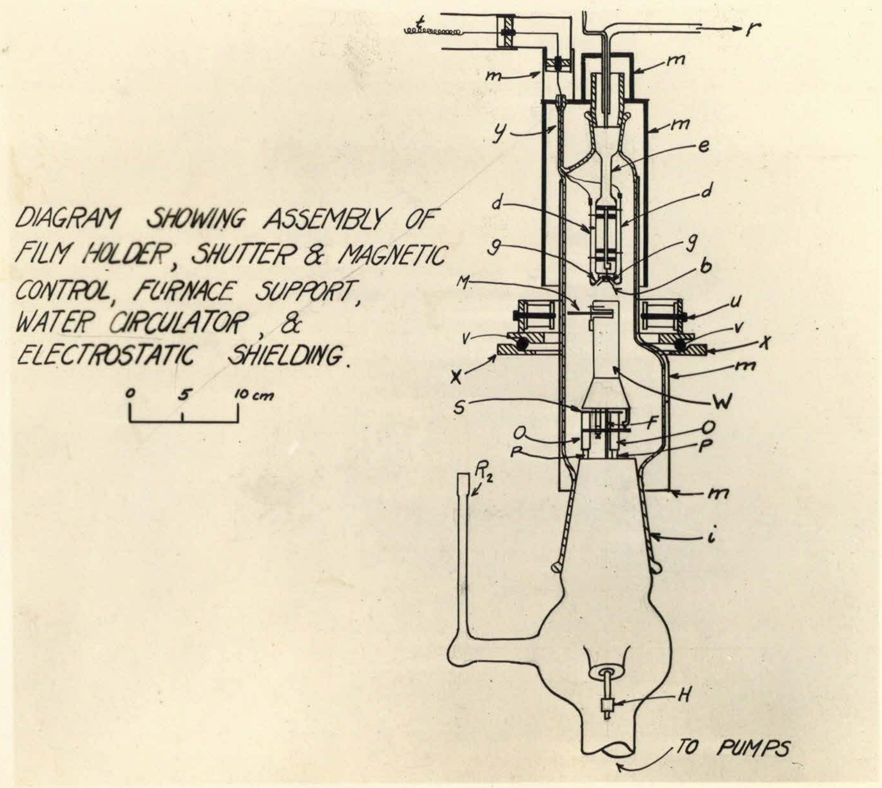
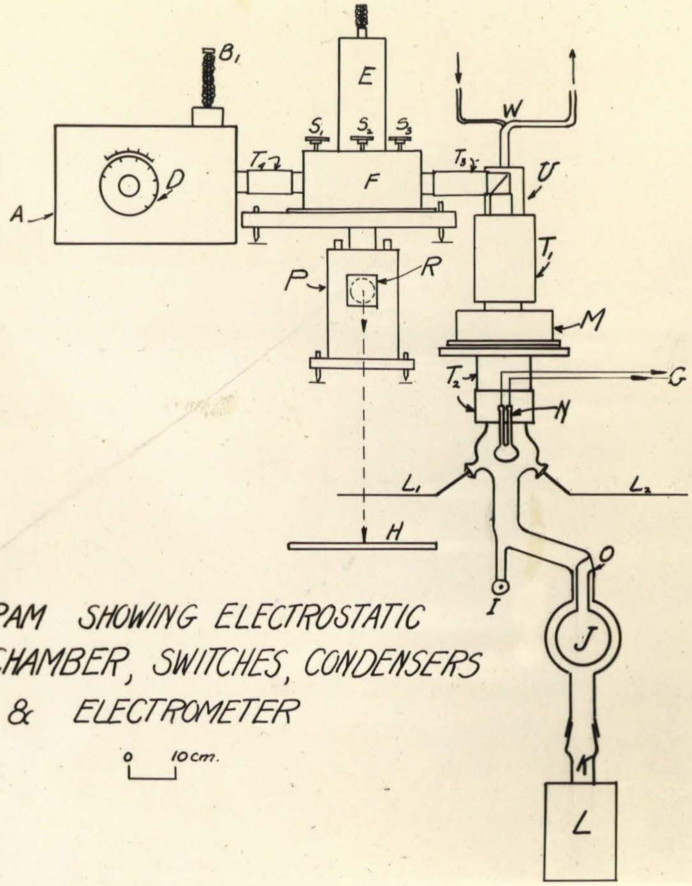


DIAGRAM SHOWING ASSEMBLY OF
FILM HOLDER, SHUTTER & MAGNETIC
CONTROL, FURNACE SUPPORT,
WATER CIRCULATOR, &
ELECTROSTATIC SHIELDING.
0
5
10 cm
t
r
m
m
m
y
e
d
d
g
g
b
M
u
v
v
X
x
m
W
S
F
O
O
P
P
m
R₂
i
H
TO PUMPS

Fig. 2



SCHEMATIC DIAGRAM SHOWING ELECTROSTATIC SHIELDING OF CHAMBER, SWITCHES, CONDENSERS & ELECTROMETER

Fig. 3

was that the one below - being too far away - did not hold enough to deposit both the bridges and the adsorbed film.

The space between the bridges - where the adsorbed film was to be deposited - was protected during their formation by a soft iron strip. This was afterwards removed with a magnet.

Constancy of the film temperature is insured by water cooling. Water is forced down the tube (n) - only the upper part is shown in the figure - to the bottom of the tube (e), where the film-backing is held; and it is sucked out by means of a water aspirator through the larger concentric tube (r).

The chamber is thoroughly shielded electrostatically. This is done in sections for convenience. They are all labeled (m).

Current for the two furnaces passes in through two leads (H) - one is behind the other. Both furnaces are mounted on the same leads.

Thermo couple wires to the lower furnace are introduced through two long capillaries R_1R_2 - one is behind the other.

Figure (3) is a schematic diagram showing the chamber in its relation to the other parts of the apparatus. $T_1T_2T_3$ and U are electrostatic shields, all of which were labeled (m) in figure 2. (M) is the rotating magnet controlling the shutter; (W) represents the water cooling leads; (N), the two capillaries for the thermocouple; and L_1L_2 the current leads to the furnaces.

(2) Detail of Crystal Holder

The crystal holder (see fig. 5 and 6) serves a fourfold purpose. It supports: the crystal; the electrodes and clamps holding the crystal; the shield which protects the space - where the adsorbed film is later deposited - between the electrodes while the metallic bridges are being deposited; and finally the slit defining the film on the backing.

These parts are all mounted on 4 rings (h) which fit tightly into grooves made in the quartz tube (e). Quartz was used as it must withstand wide variations of temperature. Each ring, made of copper and consisting of two semicircular brackets, was held securely in its groove by two tungsten springs, as shown in the diagram. Tungsten was used as it does not loose its springiness at the high temperatures used for outgasing.

The processes of holding the film-backing and making electrical connection with the film-electrodes were combined in the two clamps (g) spot welded to two rods (d) which slide through holes in brackets mounted on alternate rings (h). Tension in the clamps is maintained by using tungsten springs (f) and molybdenum elbows (g) spotwelded onto (d).

It was found imperative to have the clamps (g) make very close and even contact with the film-backing (n). A satisfactory way of accomplishing this was to spotweld very carefully onto (g), the edge of a Gem razor blade.

Even the close contact secured in using the razor blade

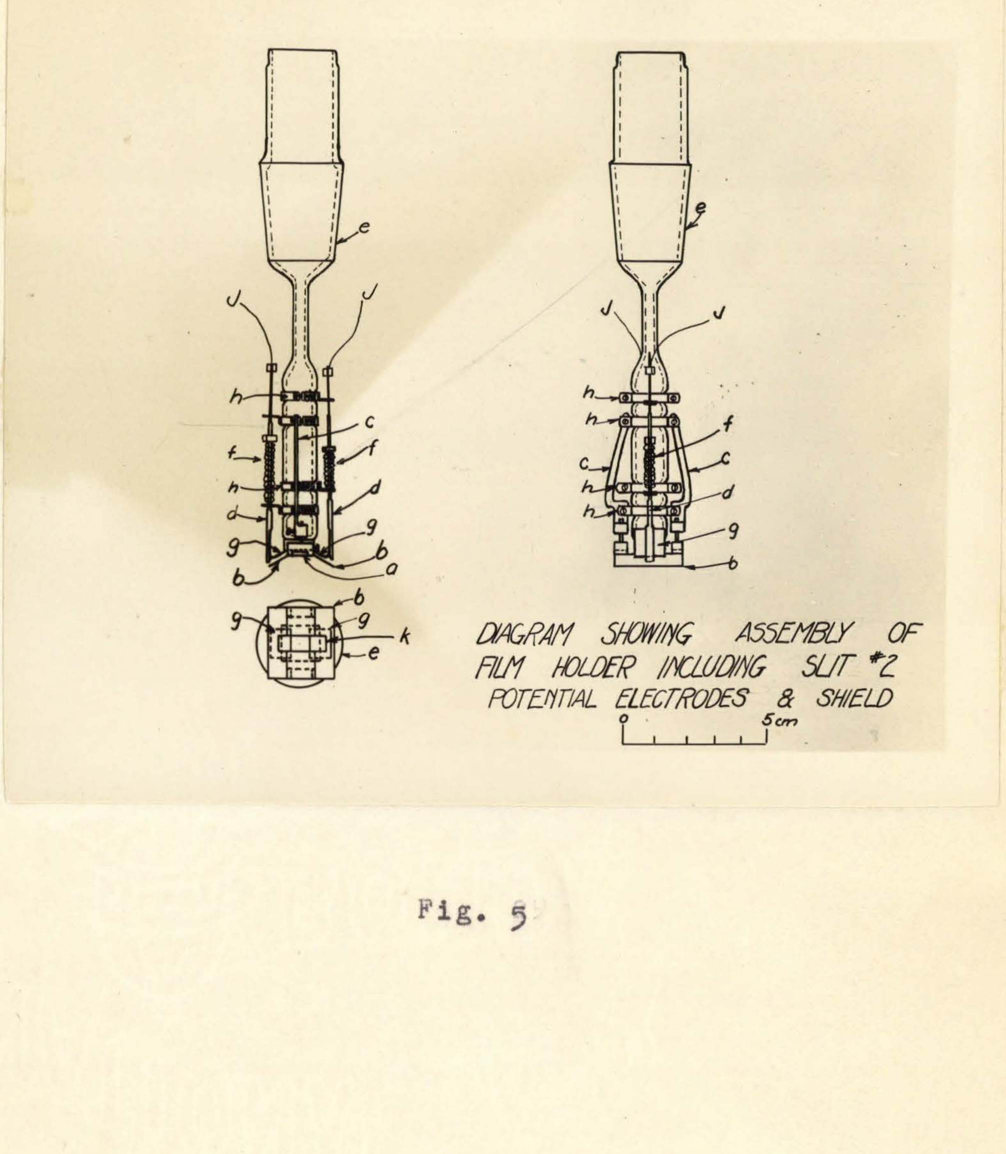


DIAGRAM SHOWING ASSEMBLY OF FILM HOLDER INCLUDING SLIT #2 POTENTIAL ELECTRODES & SHIELD

Fig. 5

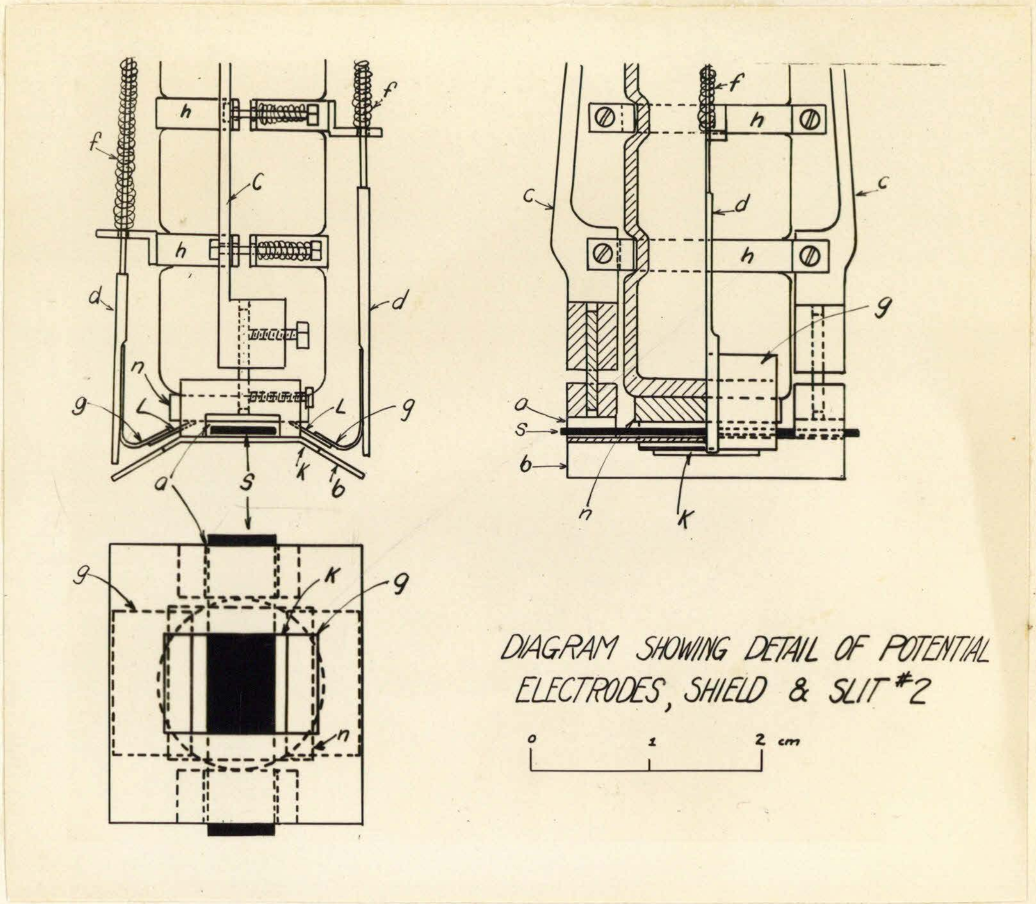


DIAGRAM SHOWING DETAIL OF POTENTIAL ELECTRODES, SHIELD & SLIT #2

Fig. 6

edges was inadequate for making dependible electrical contact with the adsorbed films. An excellent way of overcoming the difficulty was to place a shield (S) between the electrodes (L); and on each side of (S) - from the auxiliary furnace below - to deposit a heavy metallic film bridging the backing and the electrodes (L), whereafter (S) was removed by a magnet. The adsorbed layer was then deposited between the heavy metallic bridges. This method enables one to make dependable electrical contact with films of any thickness, no matter how small.

The shield supporter (b), mounted on alternate rings (h) by means of the brackets (c), is also the slit (K) which defines the size of the adsorbed layer deposited.

All of the parts except (S) are of copper, in order to enable one to remove (S) with a magnet. And all permanent joints are either spotwelded or silver soldered. (S) is made of extremely soft transformer iron and the edges of its lower side are beveled to prevent its becoming attached to (K) during the deposition of the electrodes.

(3) Details of the Shutter and the Second Slit, Defining the Surface of Evaporation.

These are shown pictorially in fig. 7 and 8. The base for the entire mounting is a candle-stick-like arrangement of glass with three arms ($c_1c_2c_3$). The whole, by means of the glass tube (D), is made an integral part of the large glass cone forming the bottom of the chamber.

Fitting into these cups are three pyrex rods (P). The tops of these rods fit into three steel cups on top of which is screwed a ring (T). This arrangement, it is found, gives a remarkably rigid foundation for the super structure.

The slit is supported by two brackets (U) and (V) screwed to the ring (S).

The shutter is supported on (W), at the bottom of which is a tripod $N_1N_2N_3$ which is screwed to the ring (S) by means of (N_3).

(W) spotwelded together from molybdenum - this metal being used as it has a very low vapor pressure at high temperatures - is the support of the shutter (M), also made of molybdenum. On the lower side of (M) is a soft iron bar by means of which (M) can be magnetically controlled from the outside.

A detail of the magnetic control is given in fig. 9. Two magnets (m) are mounted on a carriage (d) on the bottom of which is a groove (c). The whole is supported on three ball bearings (a) which roll in another groove (b) in the base plate, as shown.

The ball bearing construction was necessitated as the magnets could not be conveniently mounted on an axle.

(4) Furnaces

(a) General

Fig. 10 shows schematically their mounting. (F_1) deposits the metallic bridges; (F_2) deposits the adsorbed film; one is mounted above the other. After the bridges are deposited, the

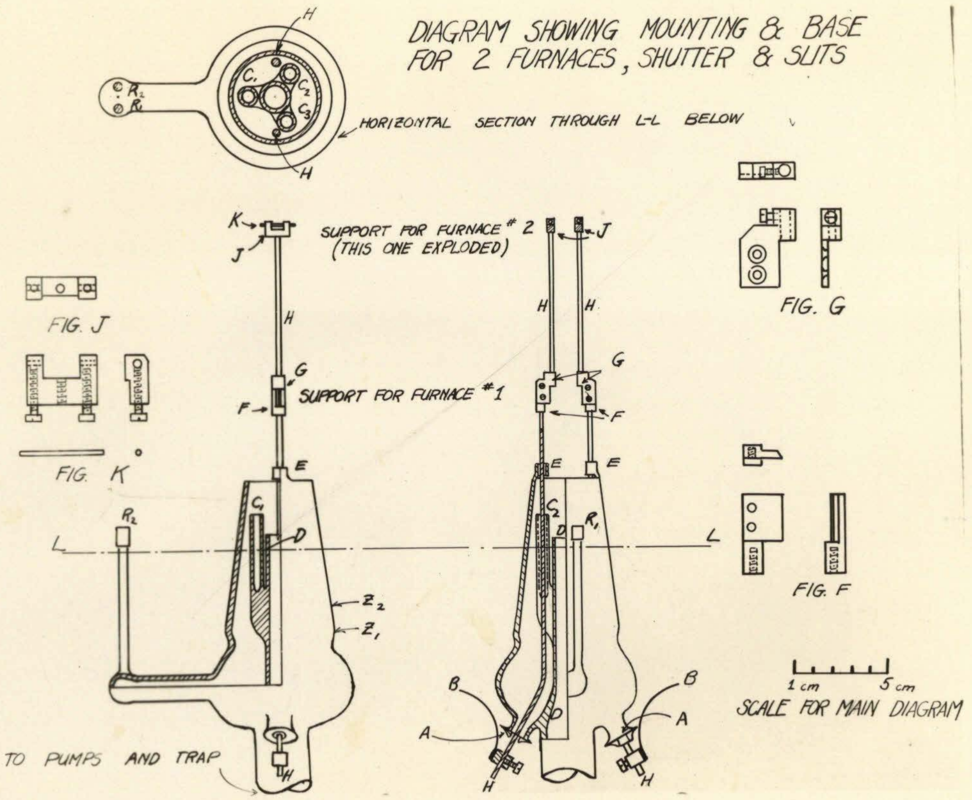


DIAGRAM SHOWING MOUNTING & BASE
FOR 2 FURNACES, SHUTTER & SLITS
HORIZONTAL SECTION THROUGH L-L BELOW
H
C_1
C_2
C_3
R_2
R_1
K
J
SUPPORT FOR FURNACE # 2
(THIS ONE EXPLODED)
FIG. J
FIG. K
FIG. G
FIG. F
H
G
F
SUPPORT FOR FURNACE # 1
E
D
L
Z_2
Z_1
A
B
TO PUMPS AND TRAP
1 cm
5 cm
SCALE FOR MAIN DIAGRAM

Fig. 7

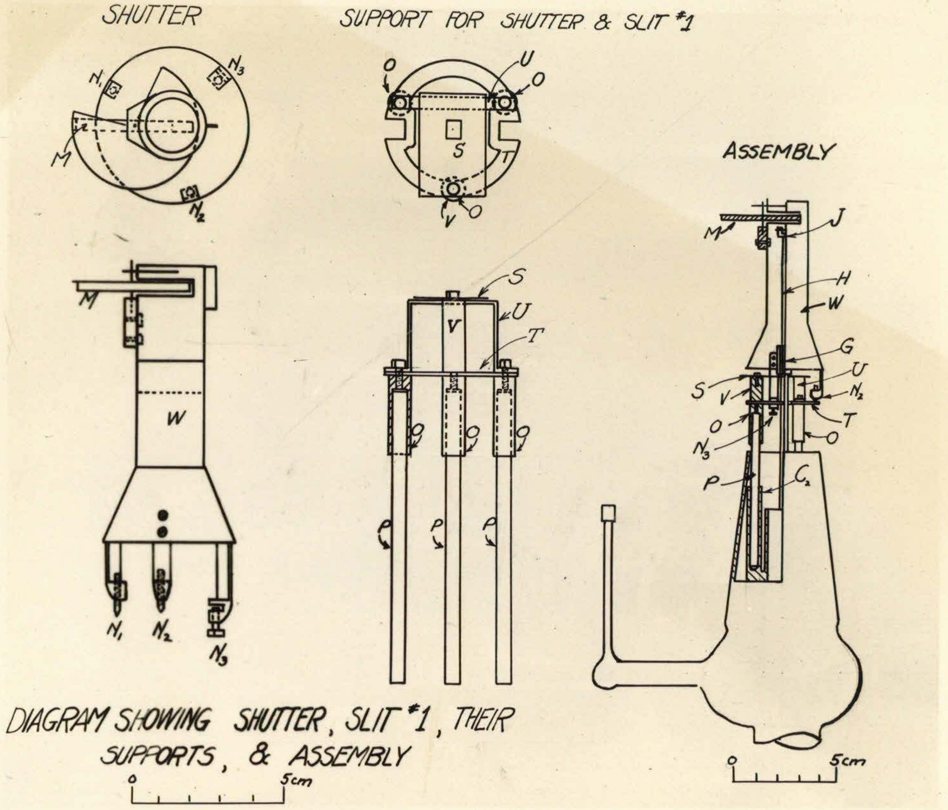

SHUTTER
SUPPORT FOR SHUTTER & SLIT #1
ASSEMBLY
N1
N2
N3
M
O
U
S
T
V
W
P
J
H
G
C2
DIAGRAM SHOWING SHUTTER, SLIT #1, THEIR SUPPORTS, & ASSEMBLY
0
5cm

Fig. 8

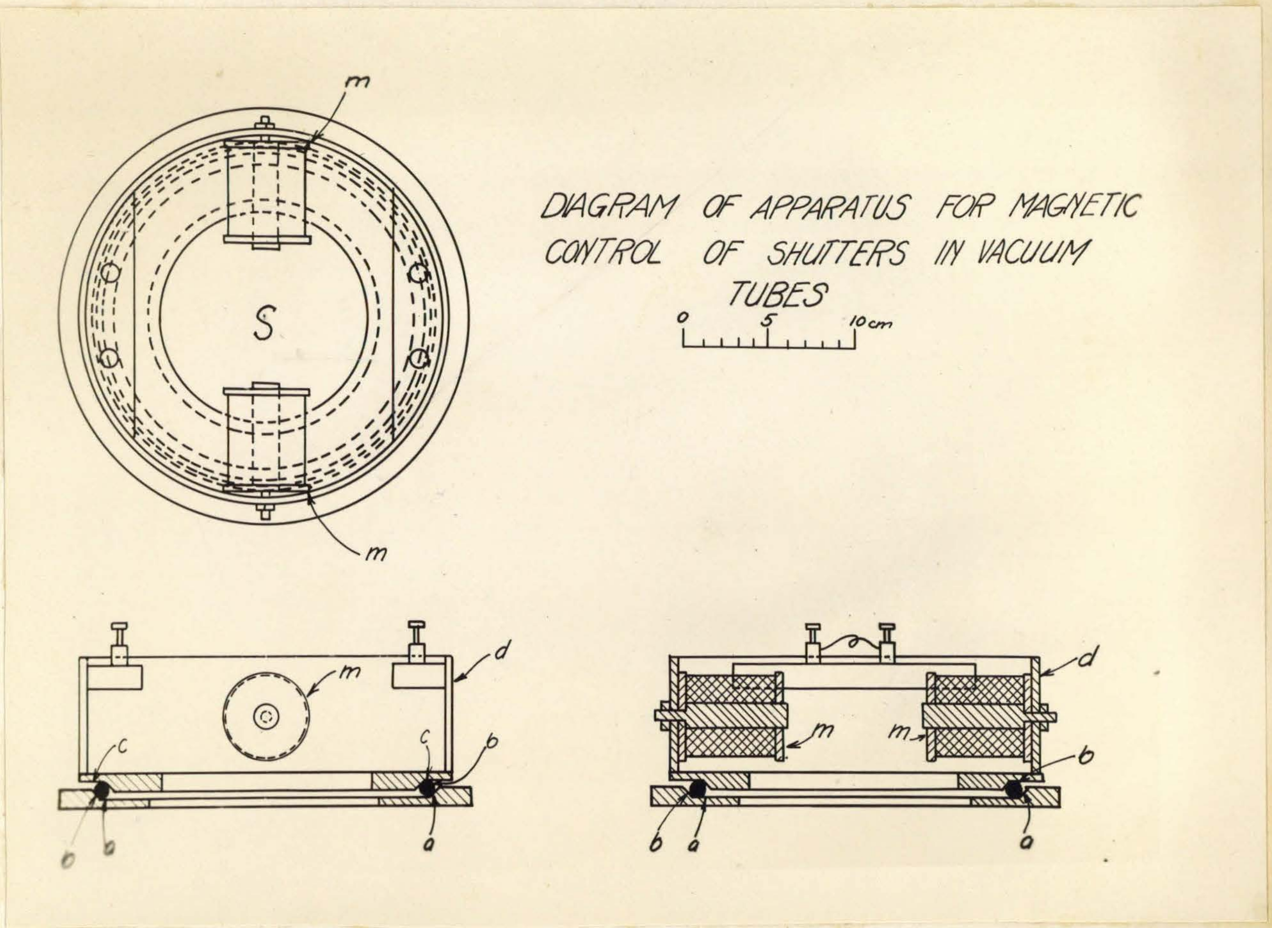
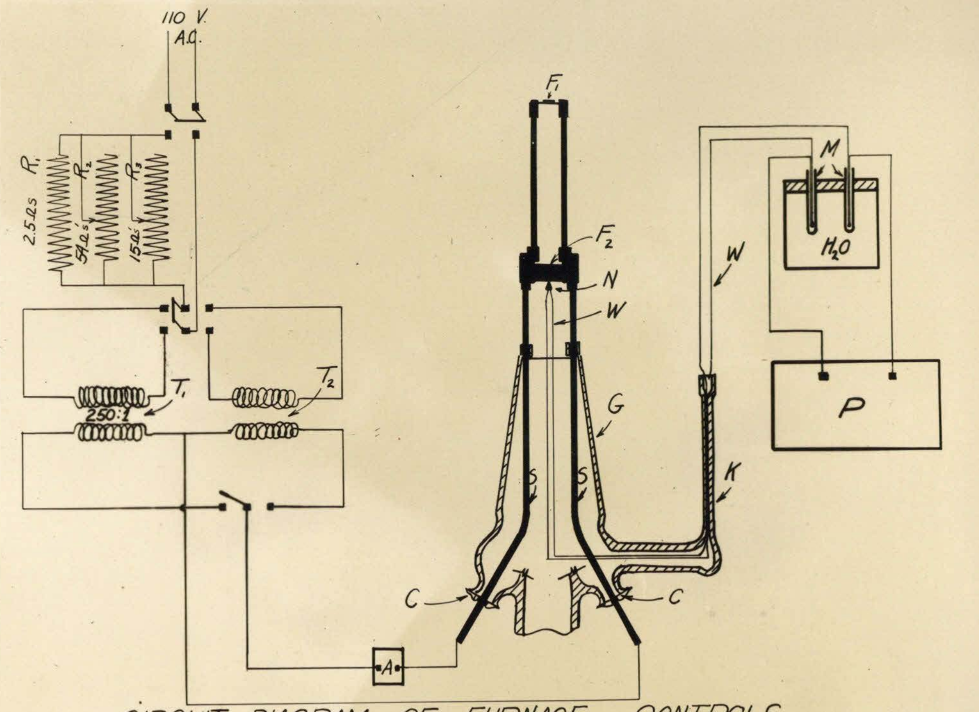

m
DIAGRAM OF APPARATUS FOR MAGNETIC CONTROL OF SHUTTERS IN VACUUM TUBES
0
5
10cm
S
m
d
m
c
c
b
b
b
a
d
m
m
b
b
a
a

Fig. 9



CIRCUIT DIAGRAM OF FURNACE CONTROLS

Fig. 10

one (F_1) is exploded and its remainder automatically removed - clearing the path between (F_2) and the film-backing - by a remarkably simple mechanical arrangement. Its removal is accomplished by having its ends pivoted or hinged on two axles (J), see Fig. 7. When (F_1) is burnt in two, each half is by gravity pulled downward about its axle.

Both furnaces (F_1) and (F_2) are mounted on the same leads; a very great advantage from the standpoint of simplifying the apparatus and economizing on space. In order to accomplish this, two conditions are to be satisfied: (1) The resistance of (F_1) must be small with respect to (F_2), so that - with the application of the same voltage - (F_1) will become very hot while (F_2) remains cool. (2) And the impedence of the exterior part of the circuit including the transformer must be the same order magnitude as that of the furnaces, which are only a few thousandths of an ohm. Otherwise one finds, both from calculation and by experiment, that the burning out of one furnace automatically entails the burning out of the other.

In order to satisfy condition (2) it is impossible to make use of the customary way of controlling the current in the primary circuit of the transformer, with a rheostat. This is because the impedance in the primary is always reflected into the secondary. Current-control by a rheostat in the secondary is also out of the question as the current is here often greater than 100 amperes.

What was done was to design and construct a special transformer with a turns ratio of about 400 : 1 ..... 6 with heavy taps in the secondary for obtaining the proper voltage. (T_1) in Fig. 10 represents the transformer schematically.

(T_1) was used only for the upper furnace; for the lower one another one (T_2) was used, with a 4:1 turns ratio, in combination with a vernier arrangement of rheostats ($R_1R_2R_3$). Only with the latter arrangement was it found possible to obtain the required precision in the control of the current for (F_2).

The temperature of (F_2) was determined by a platinum platinum-rhodium thermocouple (W) attached to the furnace; protected by the shield (N), and connected to the Leeds Northrup potentiometer (P) through the cold junction (M). The leads were brought into the apparatus through two long narrow capillaries (K) - one is behind the other in the figure - sealed at the ends with cotton and sealing wax. In order to simplify the subsequent removal of the wax, the cup was first filled with cotton; and then, on this, the wax was melted.

(b) Furnace (F_1) for Depositing Metallic Bridges.

This consisted of a strip cut from a sheet of Ni, .003" thick, in the shape shown in Fig. (11) and bent into the shape shown in Fig. (12). Its final design was the result of a great number of trials to find a furnace which: (1) would be operated by the same leads as the lower furnace (2) would be easily made, and replaced (3) would present a large area of evaporation and yet keep the melted metal (Ag in this case) from running to the cool ends, and there condensing and interfering with the subsequent removal of the furnace, (4) would have a much greater conductivity than the lower furnace, and yet require a relatively small current to explode it, and finally (5) would be easily and simply removed without requiring any mechanical parts to get out of order.

(C) Furnace F_2, For Depositing the Adsorbed Layers.

The paramount requirement of this furnace was that it be able to evaporate the metal at a uniform and reproducible rate. Other desirable characteristics were: (1) small heat capacity, in order to minimize heat disturbances during the experiment, (2) small temperature inertia, to minimize the time required to raise it to the proper temperature (3) small volume capacity adapting it to investigations with the precious metals whose price might make the investigation prohibitive, and finally (4) sturdy, and requiring little attention during its operation.

As none of the furnaces described in the literature possess the above characteristics it was necessary to develop one that did. Its final form is shown in Fig. 13 and 14. Fig.13 is a view from the top and Fig. 14 from the bottom. It was cut from a 1' x 6' strip of Ni .003" in thickness and bent and pressed into the form shown. The thermocouple protector shown in Fig. 14, also made of Ni, was spotwelded to the bottom of the crucible. That part of it that was welded to the crucible was made of .010" thick Ni, to increase the heat conductivity between the crucible

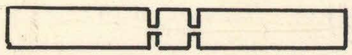


Fig. 11

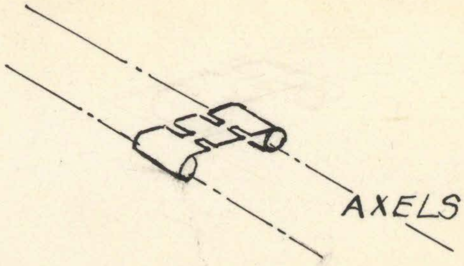


Fig . 12

Fig. 13

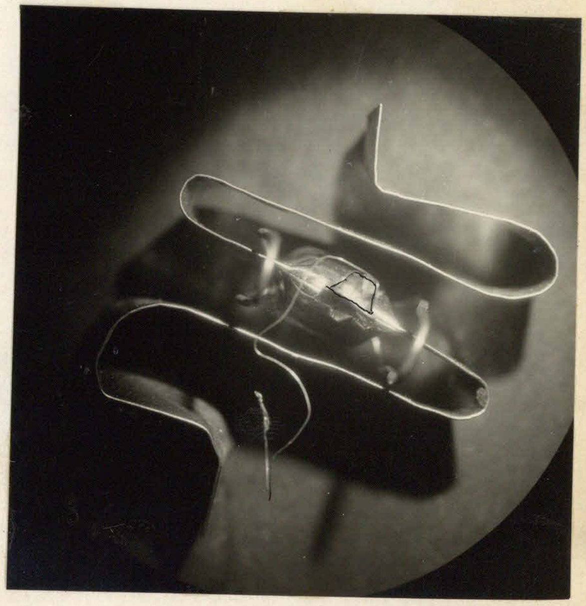


Fig. 14

and thermocouple junction. The riders shown prevented the molten metal from running off to the cooler parts of the two arms; and on the furnace in its final form, were bent so that the lower parts ran parallel to the bottom of the furnace, thus preventing secondary evaporation onto the thermocouple junction.

This type of furnace possesses an additional advantage over others. In contrast to those of the usual form, this one combines the crucible and heating element into but one unit, reducing the number of parts that might get out of order.

This furnace in its final form was the result of tests carried out on a very great number of all sizes and shapes. The uniformity in the rate of evaporation was found to be extremely sensitive to minute variations in its shape and design; and its exact form was gotten only from a continuous observation of its behavior during operation, through the walls of the glass chamber. At times a magnifying glass was necessary to bring out defects in its design. Suffice it here to enumerate the salient sources of trouble arising:

(1) Alloying: This was the first big trouble, and caused the Pt, Pt-Rh thermocouples to be dissolved off like sugar in water, no matter where they were placed.

(2) Surface tension: Would cause a dissymmetry in the surface of evaporation and pull molten metal into sharp corners and narrow crevices.

(3) Secondary evaporation: Was the process in which atoms,

condensed on a hot surface, would re-evaporate onto other parts of furnace and apparatus, causing a change of furnace characteristics and short circuiting the thermocouple leads.

(4) Gravity: In combination with surface tension and secondary evaporation onto the walls of crucible would, in time, cause a considerable deposit to collect at the bottom of the crucible. This would change the heat conductivity between the crucible and the thermocouple which, in time, it would dissolve off.

(5) The ability of molten metal to flow freely through microscopic holes. This required that parts spotwelded be kept free of holes.

(6) The tendency of molten metal to move from the hotter to the cooler parts of the furnace - caused principally by the change of surface tension with temperature - and change the temperature distribution in the furnace. The riders at the end of crucible helped overcome this difficulty.

(7) The tendency, while the furnace was being heated up, for small volcanoes to be formed around the riders and thus to pour molten metal over the sides of the crucible.

(8) The fluctuation of the thermal contact between the melt and the crucible, causing - while the temperature as determined by the thermocouple remained constant - temperature changes of the melt.

The following data shows the extreme uniformity of the rate of evaporation obtainable with this furnace. Three independent deposits of Ag at different times but under similar conditions were deposited onto the same glass plate and weighed:

		(A)	(B)	(C)
(1)	Time required for deposition in hours	3.0	3.0	6.0
(2)	Area of film in sq.cms.	.745	.688	.668
(3)	Weight of film + glass plate in grams; an average of from 5 to 10 readings	.6089458	.608904	.6089749
(4)	Weight of clean glass plate	.6089180	.608875	.6089239
(5)	Weight of film	.0000278	.000029	.000051
(6)	Rate of deposit in layers per minute	.945	1.06	.967

The weighing under (B) happened to be made during the period of earthquakes in the early part of March 1933 and might be a bit off. (A) was made after the furnace had already been in use about 15 hours. (B) was made several weeks later after the furnace had been in use a total time of about 23 hours and (C) a few days later than (B).

Comparing (A) and (C), the most dependable values and obtained at different times separated by an interval of several weeks, one finds only 2.3% deviation. Even this small deviation, I believe, is not due to the furnace but to the natural limit in the sensitivity of the microbalance. Longer time exposures or greater rates of evaporation should increase the accuracy.

As the shutter can be timed for 15 sec. exposures with a negligible amount of error, one can conclude from the above that: THE THICKNESS OF A LAYER OF MONOMOLECULAR ORDER OF MAGNITUDE CAN BE DETERMINED, WITH GREAT CARE, TO AN ACCURACY OF 3 OR 4%.

(C) Precautions Taken for Reducing the Contamination of the Film to a Minimum.

The experimental results of previous workers suffer considerably from occluded gases, which in the present work have been almost entirely eliminated. This was accomplished by a systematic cleaning and outgasing of the apparatus.

Glass ware was cleaned according to the following procedure: All parts were first dipped into hot chromic acid, then rinsed with water, and followed by nitric acid to remove all traces of metallic deposits. The parts were again rinsed in water followed by a rinse in alcohol and dried. For those parts immediately surrounding the crystal holder, ether was used instead of alcohol.

Metallic parts were cleaned in a dilute solution of nitric acid, rinsed in water, then in alcohol and dried.

The cleaning of the glass backing was carried out the same as for the glass ware above, and finally placed into a dessicator.

The crystals used as film-backing were freshly cleaved immediately before each run - without being touched with the fingers - and were then inserted as quickly as possible into the apparatus which was then immediately pumped down.

Stopcock grease was applied sparingly and confined only to a very narrow band on the outer end of the cone leaving 3/4 of that part of the cone on the side of the chamber perfectly clean.

All metal parts, especially the shutter and its attachments were thoroughly outgased at red heat by an induction furnace designed especially for that purpose. A schematic diagram of it is shown in figure 15.

(I) is the heating coil placed about the chamber; (H) the horngap, and (0) a blast of air to quench it; (K_1) and (K_2) the condensers; (D_1, D_2) choke coils and (T) the transformer.

The continued sharpness of the shadows of the parts of the apparatus in the path of the atomic rays was an indication of the high vacuum maintained at all times.

Another important factor contributing to the high vacuum was the great pumping speed obtainable with the apparatus. All tubes were of large diameter and practically no resistance was encountered at the liquid air trap (see fig. (3)).

(D) Measurement of Conductivity.

(a) General

This was done by the leakage method using an extremely sensitive string electrometer, whose current sensitivity was varied over many powers of 10 by a specially designed bank of

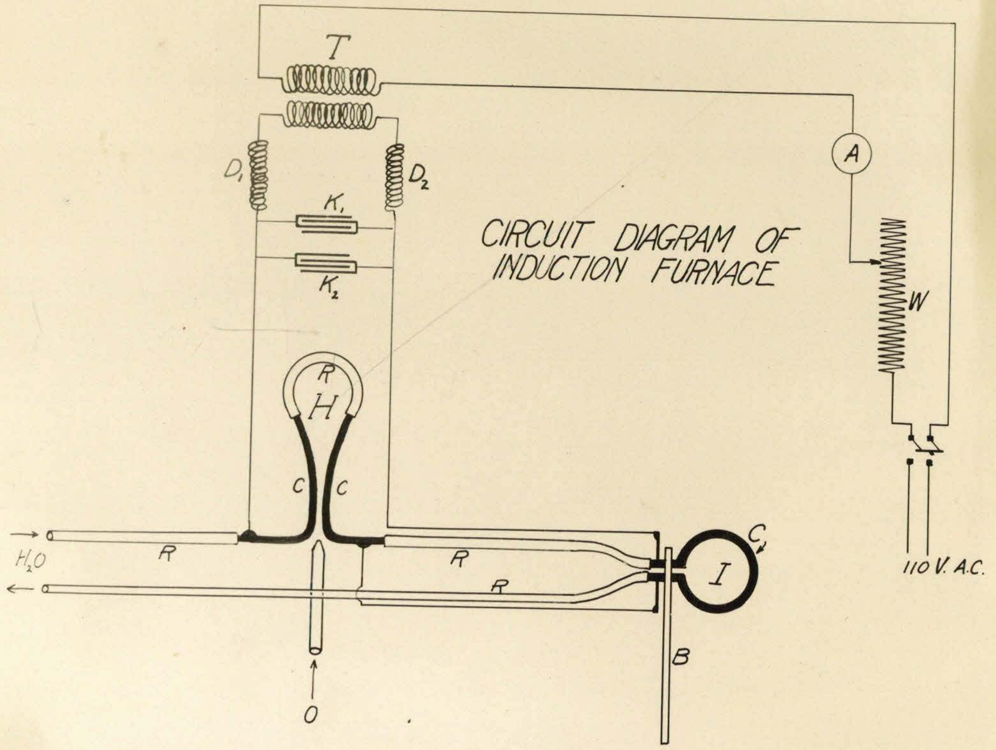

CIRCUIT DIAGRAM OF INDUCTION FURNACE
T
D_1
D_2
K_1
K_2
A
W
R
H
C
C
H_2O
R
R
R
C_1
I
B
O
110 V. A.C.

Fig. 15

condensers. The string electrometer was chosen primarily because of its extremely small capacity enabling one to measure resistances as high as 10^{15} ohms in a minimum amount of time. The capacity of the entire system is calibrated by a specially designed calibration condenser. All switches and parts are built into a single unit in order to make the electrostatic shielding as perfect as possible.

(b) Hookup

Fig. (16) is a schematic drawing showing the hookup: (K) is the film backing; (E) the electrometer; (S) a switch leading to the source of plate potential which was at all times maintained so that the fibre was at zero potential; (C_1 .. C_4) a bank of condensers whose connections with the fibre of the electrometer are made by the wire switches (S_1 .. S_4) operated by turning the dial (D). The dial (D), having four CAMS (W_1 .. W_4) which raise and lower the phosphor bronze springs (P), causes the quartz rod to open and close the switches (S_1..S_4) - according to the dial setting - enabling one to put any desired capacity in parallel with the fibre and ground. (S_1 ... S_9) are switches made of piano wire with platinum wire tips. Wire switches were used to minimize capacity changes in the system when the switches were opened and closed; and platinum tips, to eliminate contact e.m.f. (S_8) is the grounding switch, (f) is the calibration condenser, with guard rings (G), and charged up by the plunger (N). The connections are such that the guard

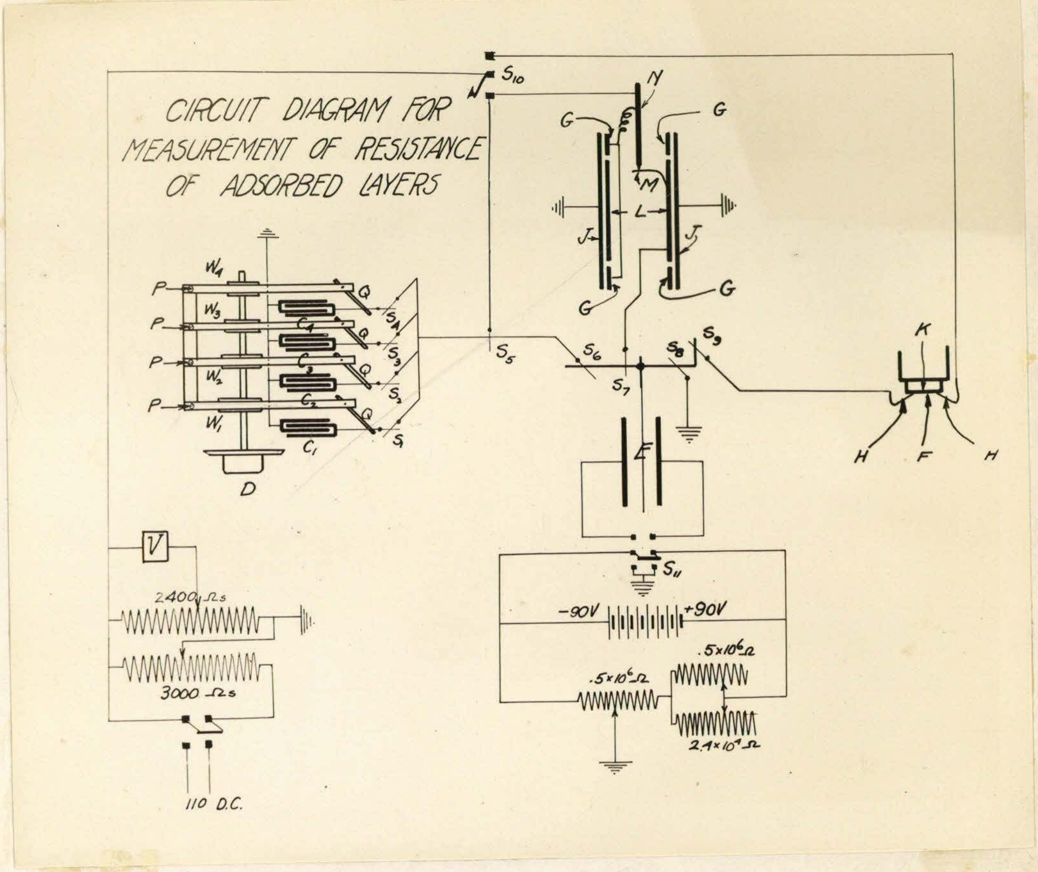

CIRCUIT DIAGRAM FOR
MEASUREMENT OF RESISTANCE
OF ADSORBED LAYERS
S_{10}
N
G
G
M
L
J
J
G
G
W_4
W_3
W_2
W_1
P
P
P
P
Q
Q
Q
Q
C_4
C_3
C_2
C_1
S_4
S_3
S_2
S_1
D
S_5
S_6
S_7
S_8
S_9
K
H
F
H
E
S_{11}
-90V
+90V
.5×10⁶ Ω
.5×10⁶ Ω
2.1×10⁴ Ω
V
2400 Ωs
3000 Ωs
110 D.C.

Fig. 16

rings are always charged to the same potential as the condenser.

Fig. (3) shows the relation of the above parts to the rest of the apparatus. (P) is the electrometer, whose fibre and scale are projected by the prism (R) onto the screen (H); (E) is the calibration condenser; (F) houses the switches operated from the outside by $S_1S_2S_3$; (T_3) and (T_4) go to the film and bank of condensers, respectively; and A, houses housing the bank of condensers manipulated by the dial (D).

(C) Method of Measuring Conductivity and Determining the Capacity of the System.

When the film-resistance is being measured S_{10} is thrown upwards placing a potential on the film; $S_5S_7S_8$ are open; S_9 is closed; and S_6 is opened or closed depending upon what electrometer sensitivity is desired.

When the voltage sensitivity of the electrometer is wanted, S_{10} is thrown downwards; S_5 and S_6 are closed; and $S_7S_8S_9$ are opened.

When the capacity of the system is to be calibrated S_{10} is thrown downward and S_5S_6 and S_8 are open. Condenser (L) is charged by (H) to a known potential. The charge is communicated by S_7 to the electrometer and the rest of the system. The new potential is determined by the electrometer.

From the known capacity and initial potential of (L), and the final potential of (L) and the system, the capacity of the system is readily determined.

Results by this method, when measuring capacities as low as

40 cm. agree within 1% of those obtained by another method developed in the course of the work. The other method makes use of the bank of condensers C_1 .. C_4 and a high resistant film. It consists in placing a standard condenser (.1 m.f.) at C_4 withe the capacities of $C_3C_2C_1$ progressively decreasing in powers of 10, and having a film of suitable resistance at (F). A fixed potential is applied to the film and the time noted that it requires the electrometer to charge up to a fixed potential, with each of the condensers - in turn - connected in. From these are found ratios between the time of leak, through the same film, for each pair of adjacent condensers. With these ratios, and the known capacity of C_4, the capacity of the system is readily determined.

(d) Detail of Calibration Condenser and Switch Housing.

Fig. 17 shows a cross section of the unit containing the calibration condenser grounding switch and other controls.

(B) leads to the bank of condensers; (F) to the film by means of the flexible piano wire spring (u). The switches (w) are of piano wire tipped with platinum wire (P) and operated by quartz rods (Q). As the grounding switch was used several thousand times during a normal run it had to be sturdy. This is brought out more clearly by the detailed sketch at the side.

(e) Detail of Apparatus for Control of Electrometer Sensitivity.

Fig. 18 shows a top view and a cross section through L_1L_2 of the arrangement used for varying the electrometer sensitivity. (D) is the dial; K_1 .. K_4 are cams; c_1 .. c_4 are condensers held

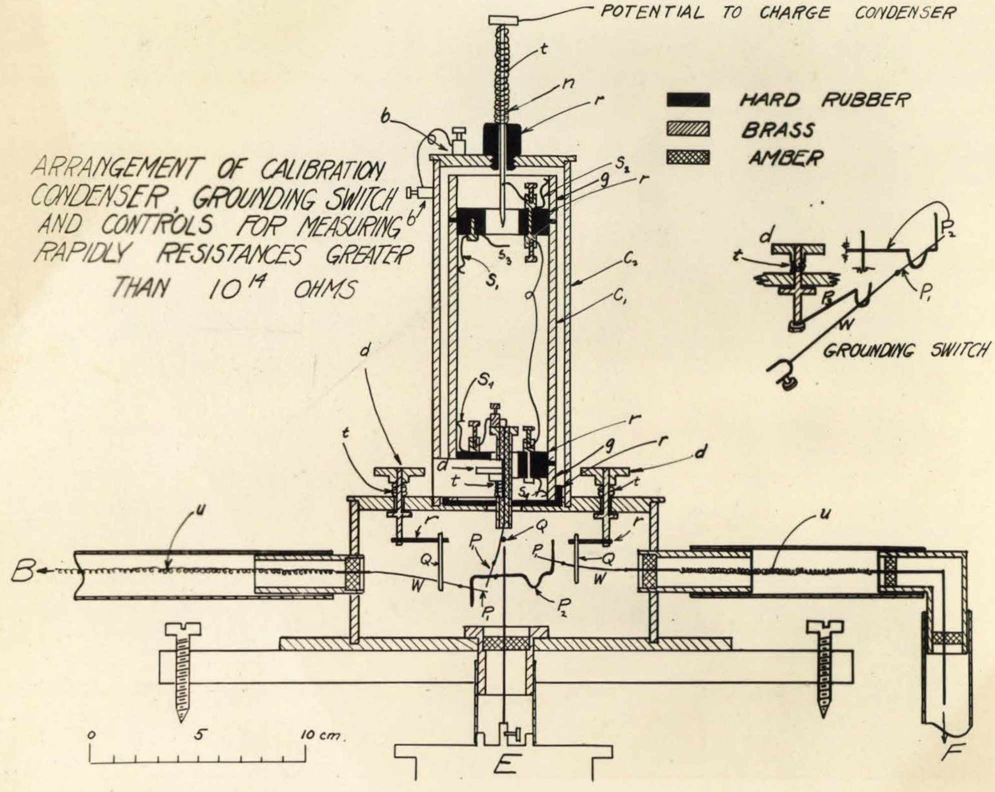

POTENTIAL TO CHARGE CONDENSER
HARD RUBBER
BRASS
AMBER
ARRANGEMENT OF CALIBRATION CONDENSER, GROUNDING SWITCH AND CONTROLS FOR MEASURING RAPIDLY RESISTANCES GREATER THAN 10^14 OHMS
t
n
r
b
b'
S2
g
r
S3
S1
C2
C1
d
S4
t
r
g
r
d
t
d
t
S4
u
u
B
r
r
Q
P1
P
Q
W
W
P1
P2
F
E
0
5
10 cm.
d
t
P2
P1
R
W
GROUNDING SWITCH

Fig. 17

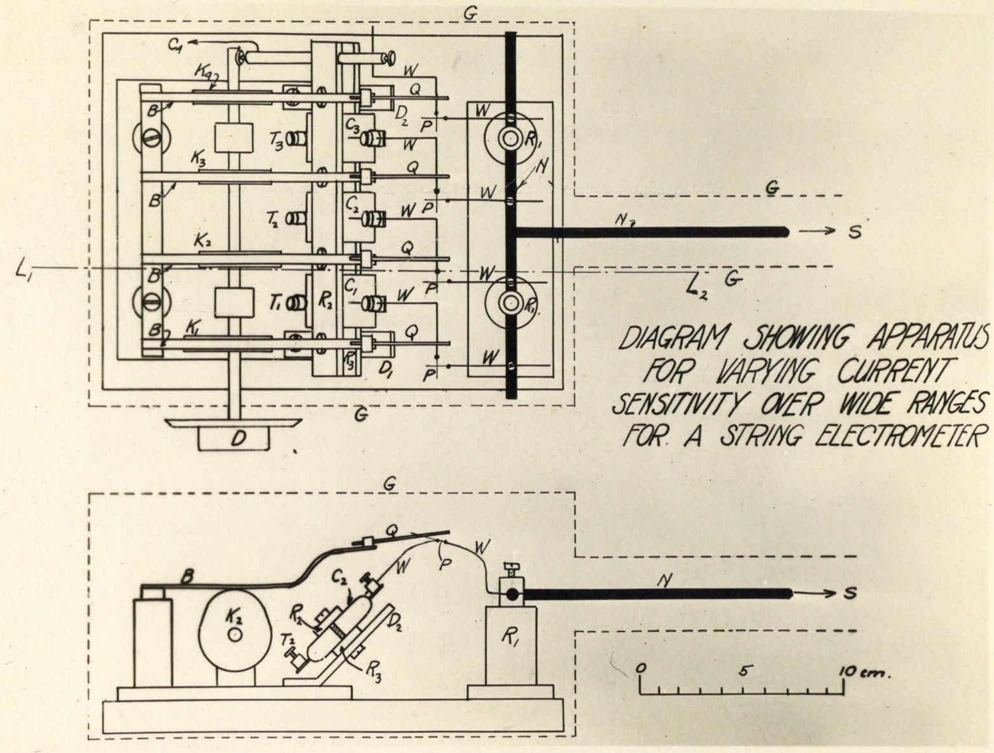


DIAGRAM SHOWING APPARATUS FOR VARYING CURRENT SENSITIVITY OVER WIDE RANGES FOR A STRING ELECTROMETER

Fig. 18

in place by hard rubber rods R_2 and R_3; the (B's) are phosphor bronze springs at whose ends are quartz rods (Q) for manipulating the wire switches.

The principle of operation of the whole arrangment can be best seen from the operation of a single condenser. Take C_2 and consider the lower diagram. As the cam (K_2) is turned into the position shown in the figure, (Q) - which normally presses against the piano wire (W) holding the switch open - now rises and allows the two wires to make contact connecting C_2 with the electrometer. The cams are so arranged on the shaft that almost any combination of condensers can be connected with the electrometer, merely by turning the dial (D).

(E) Method of Setting up the Apparatus and Taking Readings:

(a) Preliminaries:

(1) All glassware and metal parts were thoroughly cleaned according to the proceedure previously outlined, before ever the apparatus was put in use, and the chamber was cleaned before each run.

(2) Rate of evaporation of the lower furnace F_2 determined by the Mechanical Method as described on page 43 .

(3) New auxiliary furnace F_1 inserted and loaded.

(4) A freshly cleaved crystal backing inserted.

(5) Apparatus pumped down.

(6) Metal pellets in auxiliary furnace (F_1) melted down to prevent their flying off during the

application of the induction furnace.

(7) Induction furnace applied.

(8) Water circulation for the cooling of the film-backing applied

(i) Metallic bridges deposited by auxiliary furnace (F_1) in shifts of a minute or more, to prevent crystal from heating up.

(j) Auxiliary furnace exploded.

(k) Shield - for protecting space between metallic bridges above - removed.

(l) Apparatus now electrostatically shielded and magnetic shutter control put around chamber.

(b) Taking Readings

(m) Shutter closed and lower furnace (F_2) brought slowly up to the predetermined temperature.

(n) Shutter opened and backing exposed for a definite time interval in order to deposit a known number of atoms.

(o) Current to lower furnace shut off.

(p) Film resistance measured from time to time until it had approached an asymtotic value.

(q) Steps m, n, o, p repeated for each new deposit to be studied.

(r) And at no time during a run were any of the pumps stopped; they were kept going night and day.

VII Experimental Results and Conclusions.

(A) Dependence of Resistivity on Time - Extremely Thin Films on Calcite.

(a) Data, Conventions, and Definitions.

Figs. 19, 20 and 21 show the dependence of resistivity on time for extremely thin (Ag) films deposited on calcite - from 1 to 55 layers average thickness. The data from which the curves were plotted is found in section (I) of the appendix. The potential applied at all times both during the formation of the film and during the conductivity measurements was 60 volts.

The thickness of the film - in average number of layers - is computed on the basis that the (110) plane is parallel to the backing; if future investigations prove that the (111) plane is parallel, then all film thickness given in this paper are to be increased by a constant factor.

It will be noticed that instead of the resistivity of the film a quantity proportional to it is plotted. This is the product of the film resistance and the average thickness in number of layers: (R x N).

In order to bring out the trend of the coefficient of recombination (k) with time - involved in the equation $\log R = kt + c$ derived on page - log NR instead of the resistivity is plotted. And the slope of the corresponding curve is then the coefficient of recombination.

From now on the following terms will have the following meanings: By "aging" will be meant the change of resistance with time. By an "unaged film" will be meant one which has just been deposited and has had no time for its component atoms to recombine. By "extremely thin films" will be meant films with a thickness below 50 layers or so; by "thin films" will be meant films with a thickness greater than 50 layers and at least up to 330. The difference in experimental results for these two ranges will justify this distinction.

Curve (I) of fig. 19 represents the aging of a film having 1.45 layers average thickness. The slope representing the coefficient of recombination (k) is seen to be remarkably constant for the first 40 minutes or more, whereafter the resistivity approaches an assymtotic value after 1 1/2 hours or more - in the curves the aging is shown only for the initial 75 minutes.

Curve (II) represents the aging of film (I) - fully aged - with a fresh additional deposit of 0.96 layers. It is the same as (I) in every respect except that (k) the coefficient of recombination - represented by the slope of the curve - is a bit less.

Each of the succeeding curves: III ... VIII, represents the aging of the corresponding film with 0.96 layers added to the preceeding film, e.g. Curve (IV) represents the addition of 0.96 layers to (III) which is fully aged and already has a thickness of 3.37 layers, as indicated on the curve.

Fig. 20 and 21 are continuations of fig. 19 up to 53 layers, average thickness. As a means of comparison curve VIII is found in both fig. 19 and 20, and curve XVIII is found in both fig. 20 and 21. The average number of layers added to the preceeding fully aged film is indicated in brackets; and the total thickness of the film, without brackets.

(b) Aging of Extremely Thin Films.

A remarkable thing common to all the deposits is that the resistivity during the process of aging increases several hundredfold its initial value within an hour or more. None of the many previous workers have found this. They always report a decrease of resistivity with time as mentioned in the introduction. We can likewise obtain a decrease of resistivity with time if we merely turn the diffusion pump off for a short time. The subsequent few films deposited then show a decrease of resistivity with time.

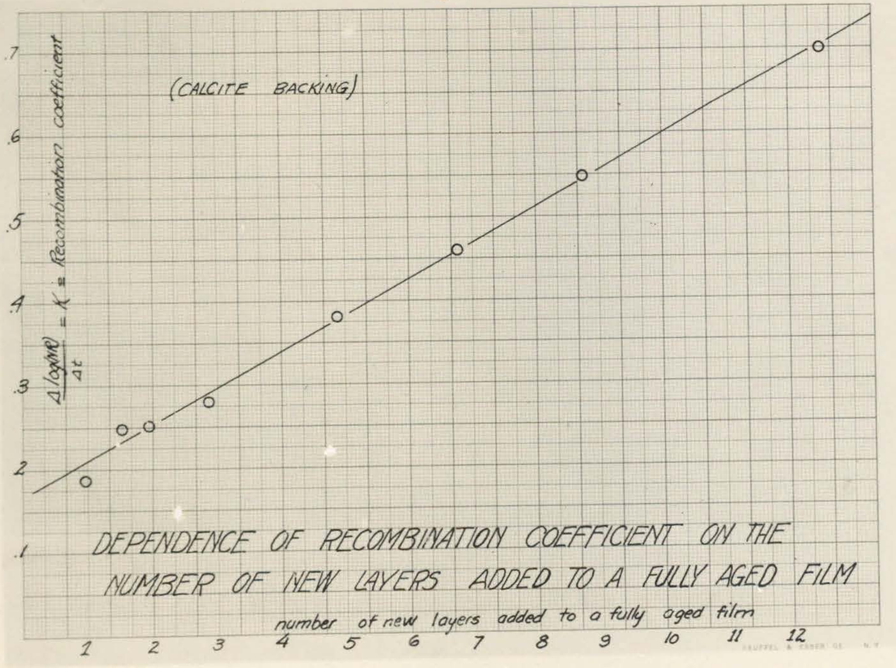
(c) Resistivity as a Function of Thickness.

Furthermore it is seen that each additional deposit tends to increase the film resistivity. This also has never been observed before. All previous workers find an infinite resistivity in this range, where we find a continuous increase.

(d) Dependence of the Recombination Coefficient on the Number of Unaged Layers Deposited at One Time.

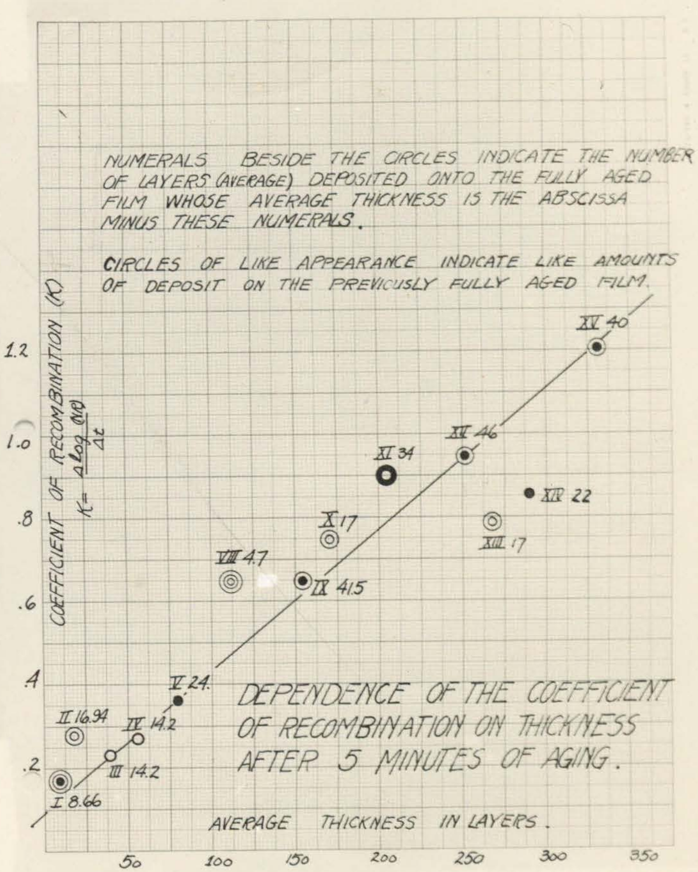
This same set of curves shows that the coefficient of recombination (k) is a constant over a considerable period of time after the film has been deposited. This is brought out by the initial straight line portion of the curves.

Also (k) is seen to be independent of film thickness and



DEPENDENCE OF RECOMBINATION COEFFICIENT ON THE NUMBER OF NEW LAYERS ADDED TO A FULLY AGED FILM

FIG. 25



NUMERALS BESIDE THE CIRCLES INDICATE THE NUMBER OF LAYERS (AVERAGE) DEPOSITED ONTO THE FULLY AGED FILM WHOSE AVERAGE THICKNESS IS THE ABSCISSA MINUS THESE NUMERALS.

CIRCLES OF LIKE APPEARANCE INDICATE LIKE AMOUNTS OF DEPOSIT ON THE PREVIOUSLY FULLY AGED FILM.

DEPENDENCE OF THE COEFFICIENT OF RECOMBINATION ON THICKNESS AFTER 5 MINUTES OF AGING.

FIG. 27

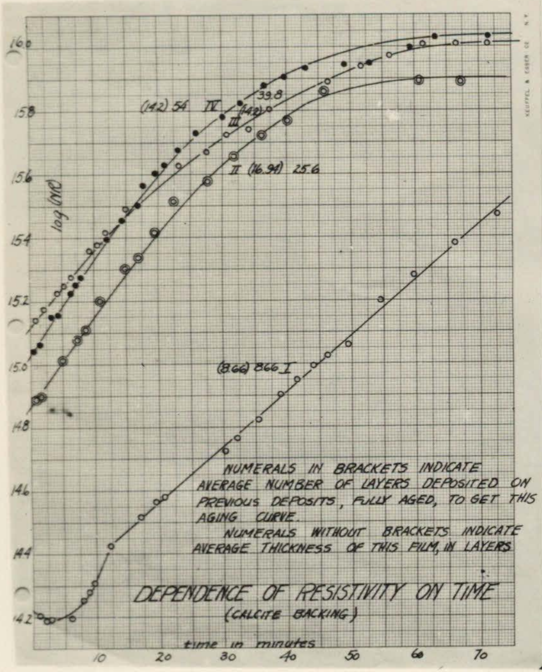


FIG. 22

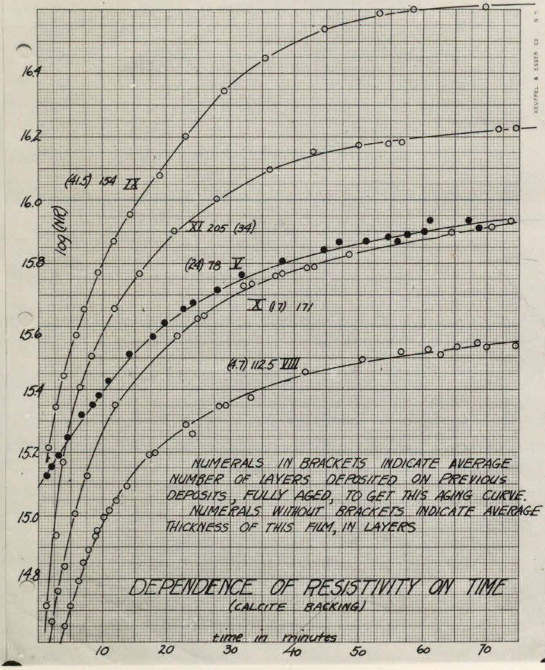


FIG. 23

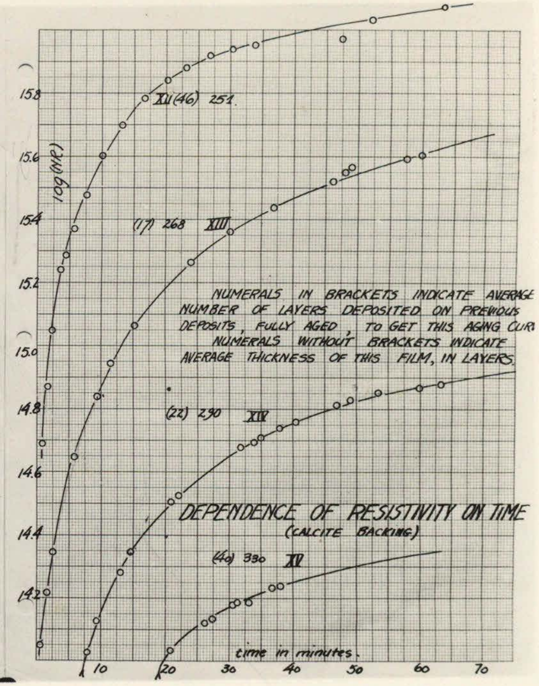


FIG. 24

depends only on the number of unaged layers initially deposited. This fact is clearly brought out if one correlates the slopes of different curves with the bracketed numbers accompanying them, particularly in fig. (19) in which one sees the remarkable parallelism of all 8 curves.

The quantitative dependence of the recombination coefficient (k) on the number of unaged layers is shown by fig. 25. (k), the slope of the curves in fig. 19, 20 and 21, is plotted against the number of unaged layers. Each point in fig. 25 represents the mean of a number of neighboring ones.

One sees that the greater the number of free and uncombined particles present the greater the rate of recombination. This fact strongly suggests that free particles on a surface obey the Mass Law.

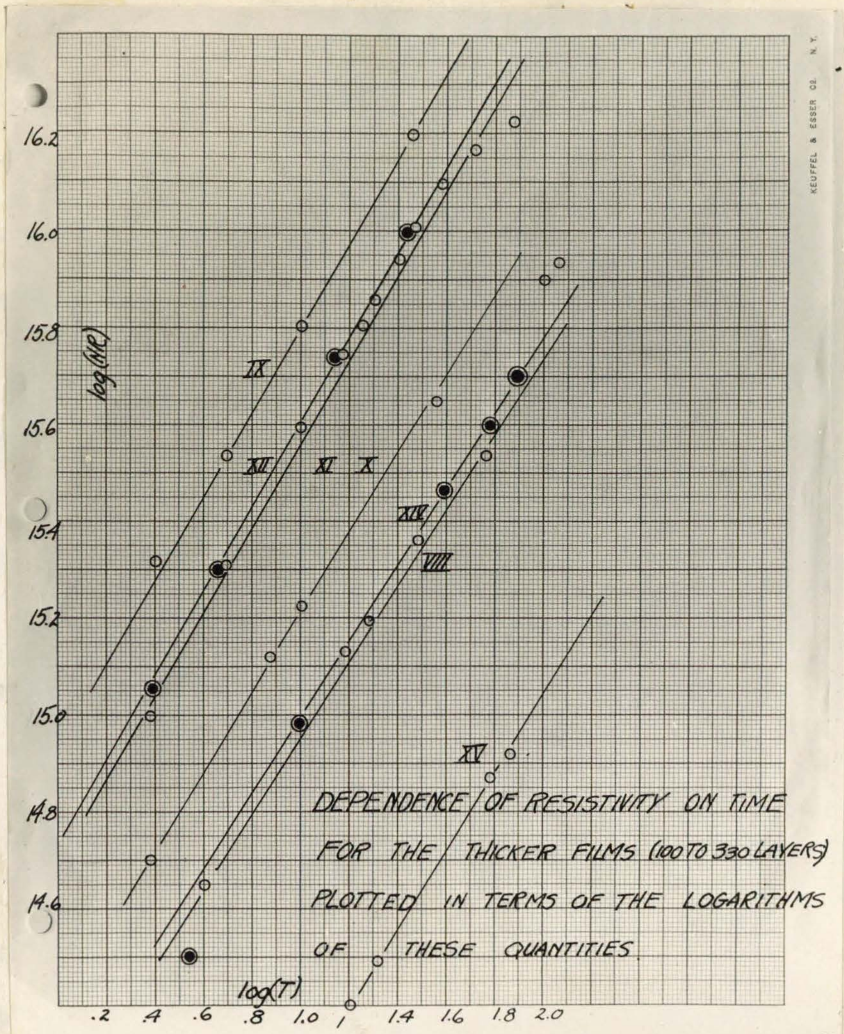
Furthermore the remarkable linearity between (k) and thickness enables one to say that $k = k'd + c'$, where k' and c' are universal constants of the film, and (d) is film-thickness.

(B) Dependence of Resistivity on Time - Thin Films on Calcite.

Fig. 22, 23 and 24 represent the aging of films with thicknesses up to 330 layers. The data from which these curves are plotted is given in section II of the Appendix. The same conventions, scale and markings apply to these curves as to the previous ones.

(a) Aging of Thin Films.

The aging of thin films (greater than 50 layers) is like


log(R/R)
16.2
16.0
15.8
15.6
15.4
15.2
15.0
14.8
14.6
IX
XII
XI
X
XIV
VIII
XV
DEPENDENCE OF RESISTIVITY ON TIME
FOR THE THICKER FILMS (100 TO 330 LAYERS)
PLOTTED IN TERMS OF THE LOGARITHMS
OF THESE QUANTITIES
log(T)
.2
.4
.6
.8
1.0
1
1.4
1.6
1.8
2.0
KEUFFEL & ESSER CO. N.Y.

Fig, 26

that of extremely thin films (less than 50 layers) in that the resistivity always increases with time; but quite unlike them, in the shape of the aging curves. We find as the thickness increases that the straight-line aging curves become parabolic. This fact is shown in Fig. 23. Curve (I) is a straight line and represents the aging of a film 8.66 layers thick, and curves VIII and IX in Fig. 24 are decidedly parabolic.

The parabolic relationship is most clearly brought out in Fig. 26 in which log (NR) is now plotted as a function of log (t) rather than of just (t). These parallel straight lines show that now R = Kt + c, where (K) and (c) are constants. There has evidently been a transition from the aging law: log NR = kt+c to: R = Kt + c.

The last relationship is exactly the one derived for thick films on page 20 on the assumption that the film was composed of a number of relatively large neighboring patches, and that these were undergoing a uniform rate of contraction in area with time.

The difference between the supposed mechanism of aging of extremely thin films and of thin films is that for extremely thin films we have the recombination of particles of comparable size; whereas for thin films, a coalescence or contraction of large patches covering most of the surface.

(b) Coefficient of Recombination of Thin Films.

(1) Dependence of Recombination Coefficient on Number of Unaged Layers.

The dependence of the coefficient of recombination on the number of unaged layers, for thin films, seems to be much the same as for extremely thin ones. Both cases show a larger coefficient of recombination with the presence of a larger number of unaged layers - or what is the same thing: with the presence of a larger number of free and uncombined particles; e.g. take points XI, XIII, XIV, XV in fig. 27. It is seen that (k) is lowest when the number of uncombined layers present is least.

This indicates that the recombinations, also in thin films, follow the Mass Law.

(2) Dependence of the Recombination Coefficient on Film-Thickness

On the other hand the dependence of (k) - the coefficient of recombination - on thickness, for thin films, is quite different from that for extremely thin ones. For thin films, refering again to figure (27), there is a decided increase of (k) with thickness, irrespective of the number of unaged layers present; for extremely thin films, (k) was independent of thickness.

(E) Dependence of Resistivity on Film Thickness - Calcite Backing

The dependence of resistivity on thickness for extremely thin films (thickness up to 50 layers) is shown in fig. (28) and for thick Thin films (thickness up to 330 layers) in fig. (29).

One sees that there is an increase of resistivity with thickness up to about 50 layers in both figures, representing results from two independent runs. Thereafter the resistivity remains approximately constant up to 250 layers, whereafter it

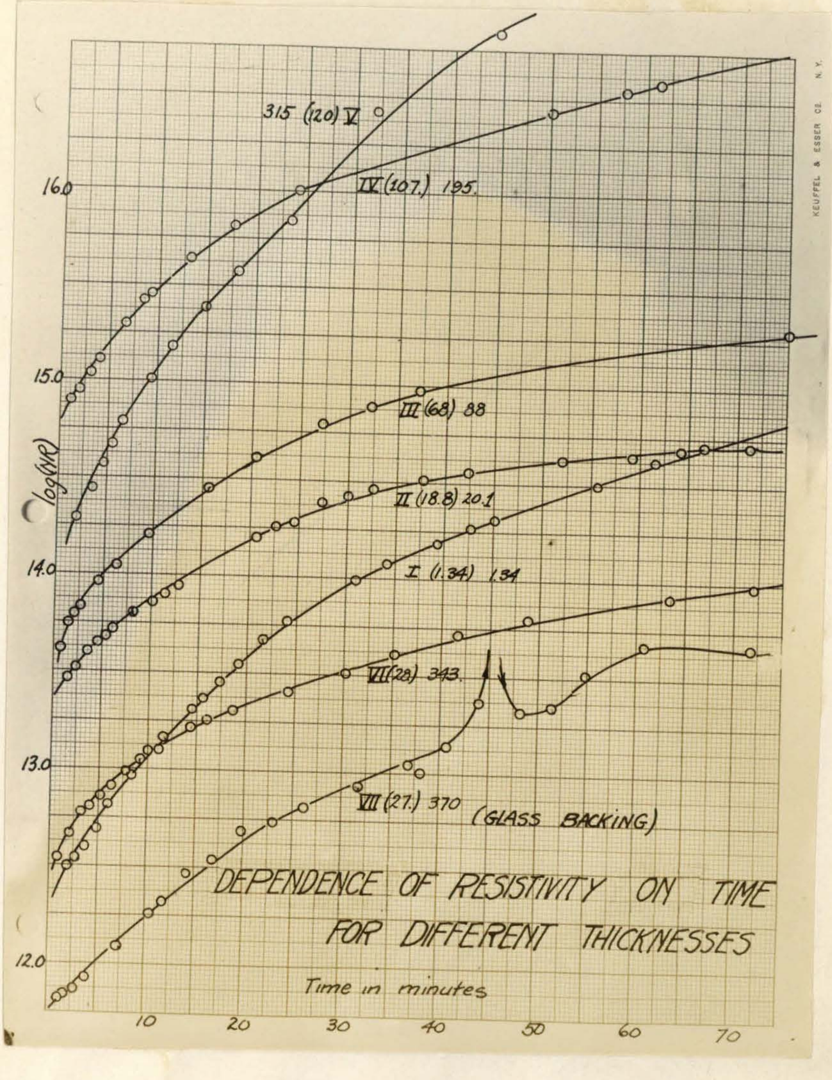

315 (20) V
IV (107.) 195.
III (68) 88
II (18.8) 20.1
I (1.34) 1.34
VII (28) 343.
VIII (27.) 370 (GLASS BACKING)
DEPENDENCE OF RESISTIVITY ON TIME
FOR DIFFERENT THICKNESSES
Time in minutes
log(1/R)
16.0
15.0
14.0
13.0
12.0
10
20
30
40
50
60
70
KEUFFEL & ESSER CO. N.Y.

Fig. 30

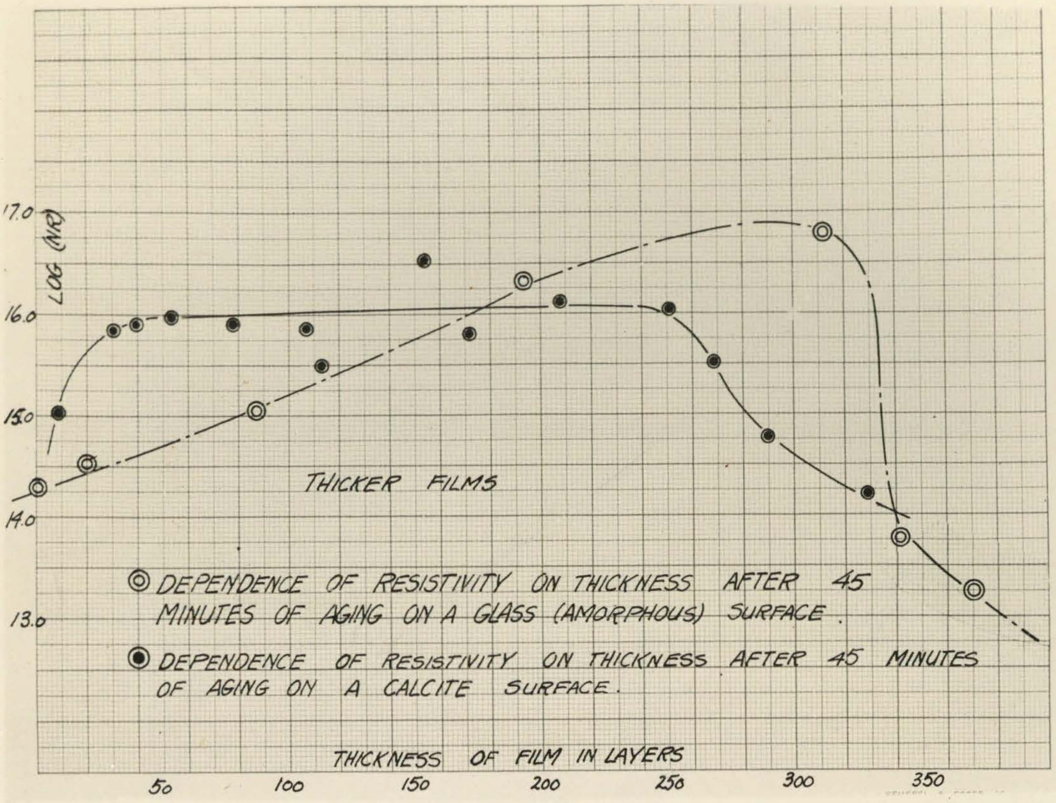

17.0
16.0
15.0
14.0
13.0
LOG (NR)
THICKER FILMS
◎ DEPENDENCE OF RESISTIVITY ON THICKNESS AFTER 45 MINUTES OF AGING ON A GLASS (AMORPHOUS) SURFACE.
● DEPENDENCE OF RESISTIVITY ON THICKNESS AFTER 45 MINUTES OF AGING ON A CALCITE SURFACE.
THICKNESS OF FILM IN LAYERS
50
100
150
200
250
300
350

FIG. 29

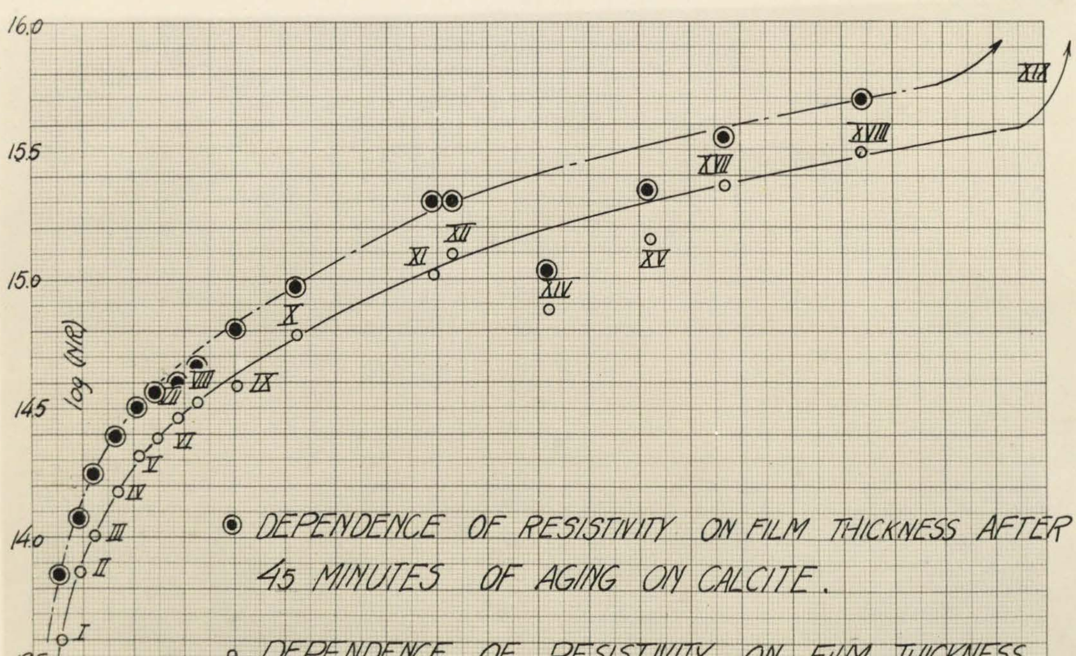

16.0
15.5
15.0
14.5
14.0
13.5
log (NR)
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIV
XV
XVII
XVIII
XIX
● DEPENDENCE OF RESISTIVITY ON FILM THICKNESS AFTER 45 MINUTES OF AGING ON CALCITE.
○ DEPENDENCE OF RESISTIVITY ON FILM THICKNESS AFTER 30 MINUTES OF AGING ON CALCITE.
THICKNESS OF FILM IN LAYERS
10
20
30
40
50

FIG. 28

suddenly drops, and would no doubt have continued to do so had the measurements been carried to greater thicknesses.

(F) Dependence of Resistivity on Time - Ag Films Deposited on Glass, on Amorphous Surface.

The dependence of resistivity on time for Ag films - with an average number of layers from 27 to 343 - deposited on glass is shown in fig. 30. The dependence is a great deal like that for calcite: Initially there is an apparent linear relationship of log(NR) and (t), which later merges into a parabolic one.

(G) Dependence of Resistivity on Thickness - Ag Films on Glass.

The dependence of resistivity on film thickness is shown in figure 29. Again, as on calcite, there is the sudden drop around 300 layers; but unlike a film on calcite, there is a continuous increase of resistivity up to 300 layers.

(H) Ohm's Law and Thin Films

It is here found that thin films do not obey Ohm's Law when by this one means that doubling the applied voltage will double the currents through the film. This statement is contrary to the findings of Perucca(50). He sputters (Au) onto a quartz fibre and happens to measure its resistance at the same voltage we use for (Ag). He finds that Ohm's Law is obeyed.

During the present investigations it was found that changing the voltage as little as 10 above or below the normal value applied to it during the run would cause as much as a thousandfold increase or decrease in the current, whether the film was deposited on glass or on calcite.

The observations made may be briefly summarized: If the film normally has been kept at a potential difference of 60 volts and the voltage is suddenly dropped to 50, then a manifold decrease in conductivity will be observed. This condition is not stable and after sometime - 10 to 15 minutes or more - the conductivity apparently rises to its former value, at least in order of magnitude. If now the voltage is brought back to 60 its conductivity invariably rises many hundred-fold its original value.

(I) General Conclusions.

The increase of resistivity with thickness - for Ag on calcite up to about 50 layers, followed by a sudden drop at 250 layers; and for (Ag) on glass, a continuous increase up to around 300 layers, followed by a sudden drop - points to the fact that the atoms deposited at random, undergo a process of agglomeration and coalescence.

Immediately after the initial deposit of atoms, a process begins in which each atom combines with its neighbor, forming nuclei over the entire surface. These nuclei in turn combine with each other until a few large isolated nuclei are formed, giving the film an abnormally high resistivity. Now, as the amount of the deposit increases, these nuclei increase in size until they become relatively large isolated patches. And finally, with increase of size, they make contact with each other, thus accounting for the decided drop in resistivity found at 250 layers.

The above picture for the mechanism of aging, was used as the basis of two formulae derived earlier in this paper, to account for the trend of resistivity with increase of time. These were: (1) for extremely thin films $\log NR = kt + C$, and (2) for thin films $R = Kt + c$. Their remarkable success in describing the experimental results is seen from a consideration of fig. 19, 23 and 26. This seems to amply justify the proposed mechanism of aging.

Such a dependence of resistivity on thickness as here found has never before been observed, as far as I know. Others invariably find an infinite resistivity up to about 25 layers. In this range we find a finite resistivity which increases with thickness.

The explanation for the disagreement of our results with those of previous investigators - besides the fact that their experimental methods were open to grave criticisms, as pointed out in the introduction - lies partly in the fact that theirs were obtained from unstable films that had been allowed no time to age.

To be sure the critical thickness - approximately the same for (Ag) on both glass and calcite - at which the decided drop of resistivity occurs is only about 1/3 the thickness of the "Zwicky Block", for (Bi). But one must remember that there are no doubt variations of its size with the kind of metal; and most important of all: the patches on the surface are probably not flat disks at all, but pyramids. Now the volume of these are 1/3 that of a disk of the same height. This places the critical thickness found for (Ag) extraordinarily close to the size of the "Zwicky Block".

Additional justification of the pyramid structure is that the resistivity of the film on the latter part of the resistivity-thickness-curve, beyond the critical thickness, is many thousand-fold that of the bulk metal. No doubt if the deposit had been increased sufficiently, the resistivity would have come very close to that of the bulk metal, and the pyramids would in time have become disks.

Hamburger(35) has derived a formula for the structure of thin films on strictly probability considerations, assuming that there are no force fields surrounding the atoms, which might affect the motions of the atoms on the surface. The present results show such an assumption is entirely erroneous, and cannot but lead to fallacious conclusions.

In fact by its use I haven't been able to get anything but decidedly negative resistivities for extremely thin films, which as the thickness increases becomes abnormally high positively.

Contrary to the statements of everyone else, as far as I know, who has studied conductivity as a function of thickness, I do not believe that thin films have abnormally high resistivities. I believe that the patches of which the film is composed, have a resistivity quite comparable with that of the bulk metal. On the basis of the film structure here postulated it is quite evident that the resistivity one measures is not simply that of the film but is really a combination of two resistances: (1) the high resistance of the backing, and (2) of the metallic patches, In just what proportion each of these two contribute to the resultant resistance was shown previously, in the derivation of the formula $R = Kt + c$.

For all thicknesses of films, at least up to 330 layers of Ag on calcite, there is a definite dependence of the coefficient of recombination on the number of unaged or uncombined atoms deposited onto a surface. The general conclusion is that the rate of recombination increases with the number of uncombined atoms present. This seems to be none other than the well known Mass Law applied to thin films.

For extremely thin films we found that $k = k'd + c'$, in which (k') and (c') were universal constants for the film and (d) was the film thickness. This permits us to transform the aging formula $\log (NR) = kt + C$ so as to apply to all film thicknesses and containing but one arbitrary constant (C), instead of two as $\log NR = t(k'd + c') + C$ formerly.

This expresses the dependence of resistivity on both time and thickness, with but one arbitrary constant.

There is a decided dependence of the coefficient of recombination on thickness for the thicker films above approximately 50 layers, but none below this. The general conclusion to be drawn is that for a small deposit the sublayers do not have much influence on the recombination coefficient, and that the reaction is determined principally by the number of available particles; whereas for larger deposits above 50 or 60 layers, both the sublayers, and the number of available particles exert a decided influence on the rate of reaction or the so-called recombination coefficient.

Summary

Improved experimental methods have been developed enabling one: (1) to deposit metallic films by evaporation with a greater freedom from film-contamination than hitherto ever attained, (2) to measure film resistance up to 10^{15} ohms, and (3) to determine film-thickness, of monomolecular order of magnitude, within an accuracy of 3 or 4%.

With this apparatus it was possible to obtain experimental results radically differing from those by previous workers. It is shown that their results are easily obtained when extreme care is not taken in the elimination of foreign atoms.

It is found (for Ag deposited on both calcite and glass) that resistivity increases with thickness up to 250 layers, (within the same order of magnitude as the size of the Zwicky Block) and then very suddenly drops. This is accounted for on the basis of a coalescence of the atoms into granules.

On the basis of hypotheses made as to the structure of extremely thin films, two formulae are derived describing the aging effect. For thin films: $\log R = kt + c$; for thicker films (greater than 50 layers): $R = Kt + c$, where k, K, and c are constants and (k) is the coefficient of recombination.

It is found that the coefficient of recombination increases with the number of available uncombined particles, indicating that the recombinations on a surface are governed by the Mass Law.

From the dependence of the coefficient of recombination on thickness for extremely thin films it is found that $\log NR = kt + c$ can be expressed as $\log(NR) = (k'd + c')t + c$ where k' and c' are universal constants for the film; where (d) is the film thickness; (N) the thickness of the film in layers; and (c) an additive constant of integration.

The recombination coefficient seems to be independent of thickness when film is less than (50) layers in thickness but starts to increase decidedly when the film-thickness is greater. This indicates that the sublayers exert an increasing effect on the rate of recombination of atoms, as the thickness of the sublayers increases.

And, finally, Ohm's Law does not hold for thin films.

Acknowledgements

It is a pleasure to tender to Dr. Goetz my best thanks for suggesting this problem and for his sustained interest during the course of the investigations.

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